International Fertilizer Industry Association

Micronutrients for Sustainable Food, Feed, Fibre and Bioenergy Production

R.W. Bell and B. Dell

Micronutrients for Sustainable Food, Feed, Fibre and Bioenergy Production

R.W. Bell and B. Dell

International Fertilizer Industry Association (IFA)
Paris, France, 2008

The designation employed and the presentation of material in this information product do not imply the expression of any opinion whatsoever on the part of the International Fertilizer Industry Association. This includes matters pertaining to the legal status of any country, territory, city or area or its authorities, or concerning the delimitation of its frontiers or boundaries.

Micronutrients for Sustainable Food, Feed, Fibre and Bioenergy Production
First edition, IFA, Paris, France, December 2008

ISBN 978-2-9523139-3-3

The publication can be downloaded from IFA's web site.
To obtain paper copies, contact IFA.

International
Fertilizer Industry
Association

28, rue Marbeuf,
75008 Paris, France
Tel: +33 1 53 93 05 00
Fax: +33 1 53 93 05 45/ 47
publications@fertilizer.org
www.fertilizer.org

Printed in France
Layout: Claudine Aholou-Putz, IFA
Graphics: Hélène Ginet, IFA

Table of Contents

About the book and the authors

This book is written for practitioners and stakeholders in the fertiliser industry and for policy makers whose decisions may impact on the use of micronutrients in agriculture, horticulture and forestry. The aim of the book is to:

- Explain the growing importance of micronutrients in balanced fertilisation;
- Consider the micronutrient fertiliser types that are currently available and how to best use them;
- Assess the current market and prospects for micronutrient fertilisers; and
- Discuss the policy, regulatory and quality control framework needed to maximize the benefits from using micronutrient fertilisers.

Richard Bell

Richard Bell is Professor in Sustainable Land Management at the School of Environmental Sciences, Murdoch University, Western Australia. Richard Bell is a soil fertility and land management specialist with lecturing and research experience in Australia, Bangladesh, Cambodia, China, Fiji, Indonesia, Sri Lanka, Thailand and Vietnam. His particular interests are in plant nutrition on problem soils, diagnosis and prognosis of mineral disorders of plants, plant adaption to mineral stress, crop nutrient management, rehabilitation of degraded land, sustainable land use and agricultural development in developing countries. Richard Bell is the author of 130 peer reviewed papers and editor or author of nine books. Much of his published work has been on micronutrients in plant and crop nutrition, with contributions to boron nutrition of crops and plants most noteworthy from this work. He has co-edited three volumes on boron in soils and plants and co-authored several review papers on boron. He is the supervisor of eight current and 29 completed PhD and Masters students.

Bernard Dell

Bernard Dell is Professor and Head of Plant Sciences at the School of Biological Sciences and Biotechnology, Murdoch University, Western Australia. His research in plant nutrition has been undertaken with many colleagues and graduate students in Australia, East and South-east Asia over the past 25 years. His research has encompassed establishment of visual symptoms of deficiency, setting critical values for diagnosis of deficiency, correction of micronutrient and macronutrient deficiencies in the field, improving fertiliser use efficiency by inoculation with beneficial soil organisms, improving the micronutrient density of seed, and studies on micronutrient function in plant development. Bernard Dell has studied a wide range of crop types, including grain legumes, cereals, oil crops and industrial tree crops. He has written approximately 200 scientific journal articles, a number of books and book chapters. He regularly consults for the plantation sector on all matters affecting the health of perennial crops. The most frequent constraint to productivity that he encounters in the field is the lack of application of micronutrient fertilisers.

Acknowledgements

The authors gratefully acknowledge financial assistance from the International Fertilizer Industry Association (IFA) with the preparation of the manuscript. They further acknowledge the contribution of Ms Angela Bunoan-Olegario and Mr Patrick Heffer (IFA) for assembling the market and policy information reported in Chapters 9 and 10 after surveying members of IFA internationally; the valuable reviews and careful editing of the penultimate drafts provided by Dr John Mortvedt and Mr Graham Price; and assistance provided by Dr Yashpal and Mr Harry Eslick in gathering relevant references for review. Ms Janet Box assisted in checking citation of references and final proofs.

List of scientific names for species mentioned in the text

Common name	Scientific name
Plant species	
Almond	*Amygdalus communis*
Apple	*Malus domestica*
Astragulus	*Astragulus sinicus*
Avocado	*Persea americana*
Barley	*Hordeum vulgare*
Bean	*Phaseolus vulgaris*
Bell pepper	*Capsicum annuum*
Black gram	*Vigna mungo*
Bluegum	*Eucalyptus globulus*
Broccoli	*Brassica oleracea* var. *italica*
Brussel sprouts	*Brassica oleracea* var. *gemmifera*
Cabbage	*Brassica oleracea* var. *capitata*
Canola	*Brassica napus*
Cassava	*Manihot esculenta*
Cauliflower	*Brassica oleracea* var. *botrytis*
Chickpea	*Cicer arietinum*
Clover	*Trifolium subterraneum/Trifolium repens*
Coffee	*Coffea arabica/Coffea canephora*
Corn/maize	*Zea mays*
Cotton	*Gossypium hirsutum*
Cowpea	*Vigna unguiculata*
Cucumber	*Cucumis sativus*
Durum wheat	*Triticum durum*
Flax/linseed	*Linum usitatissimum*
Grape	*Vitis vinifera*
Green gram	*Vigna radiata*
Kiwi	*Actinidia deliciosa*
Lentil	*Lens culinaris*
Lettuce	*Lactuca sativa*
Lucerne/alfalfa	*Medicago sativa*
Mango	*Mangifera indica*
Mung bean/green gram	*Vigna radiata*
Mustard	*Brassica juncea*
Narrow-leaf lupin	*Lupinus angustifolius*

Nectarine	*Prunus persica*
Norway spruce	*Picea abies*
Oat	*Avena sativa*
Oil palm	*Elaeis guineensis*
Olive	*Olea europea*
Orange	*Citrus sinensis*
Pea	*Pisum sativum*
Peanut	*Arachis hypogaea*
Pears	*Pyrus communis*
Pecan	*Carya illinoensis*
Pomelo	*Citrus maxima*
Potato	*Solanum tuberosum*
Rapeseed/oilseed rape	*Brassica napus*
Rice	*Oryza sativa*
Roses	*Rosa* spp.
Rutabaga	*Brassica napobrassica*
Rye	*Secale cereale*
Sorghum	*Sorghum vulgare*
Soybean	*Glycine max*
Spinach	*Spinacia oleracea*
Strawberry	*Fragaria vesca*
Sugar beet	*Beta vulgaris*
Sugar cane	*Saccharum officinale*
Sunflower	*Helianthus annuus*
Thale cress	*Arabidopsis thaliana*
Tobacco	*Nicotiana tabacum*
Tomato	*Lycopersicum esculentum*
Wheat	*Triticum aestivum*

Animal species

Cattle	*Bos taurus*
Frog	*Xenophus laevis*
Goat	*Capra aegagrus hircus*
Pig	*Sus scrofa domestica*
Poultry (chicken)	*Gallus gallus*
Rat	*Rattus norvegicus*
Sheep	*Ovis aries*
Zebrafish	*Danio rerio*

Acronyms, symbols and abbreviations

(as used in this book)

Acronyms

AAPFCO	Association for American Plant Food Control Officials
ANDA	Associação Nacional para Difusão de Adubos (Brazilian fertilizer industry association)
AFSA	Australian Fertiliser Services Association
CEN	European Committee for Standardization
CIMMYT	International Maize and Wheat Improvement Centre
EEC	European Economic Community
EU	European Union
FAO	Food and Agriculture Organization of the United Nations
FIFA	Fertiliser Industry Federation of Australia
ICA	International Copper Association
IFA	International Fertilizer Industry Association
IFDC	International Fertilizer Development Center
IFPRI	International Food Policy Research Institute
ISRIC	World Soil Information
ISSS	International Soil Science Society
IZA	International Zinc Association
IZiNCG	International Zinc Nutrition Consultative Group
MAFF	Ministry of Agriculture, Fisheries and Forests
NASAA	National Association for Sustainable Agriculture Australia
SDA	Secretariat of Agribusiness Defense, Brazil
TFI	The Fertilizer Institute
UNIDO	United Nations Industrial Development Organization
USEPA	United States Environmental Protection Agency
USFNB	United States Food and Nutrition Board
WHO	World Health Organization

Symbols

Al	Aluminium
As	arsenic
B	boron
$B(OH_4)^-$	borate
C	carbon

Ca	calcium
$CaCl_2$	calcium chloride
$CaCO_3$	calcium carbonate
$Ca(NO_3)_2$	calcium nitrate
Cd	cadmium
Cl	chlorine
Co	cobalt
CO_2	carbon dioxide
Cr	chromium
Cu	copper
$CuFe_2O_4$	cuprous ferrite
$Cu(OH)^0{}_2$	copper hydroxide
$CuSO_4.5H_2O$	copper sulphate
F	fluorine
Fe	iron
Fe(III) to Fe(II)	reduction of ferric to ferrous ion
$Fe(NO_3)_3.9H_2O$	ferrous nitrate
$Fe_2O_3.9H_2O$	ferrihydrite
$Fe_3(PO_4)_2.8H_2O$	vivianite
FeS	iron sulphide
$FeSO_4$	ferrous sulphate
HCl	hydrochloric acid
HCO_3^-	bicarbonate ion (hydrogen carbonate)
Hg	mercury
H_2O_2	hydrogen peroxide
H_2SO_4	sufuric acid
I	iodine
K	potassium
KCl	potassium chloride
KH_2PO_4	potassium dihydrogen orthophosphate
Mg	magnesium
Mn	manganese
Mn(II)	manganous ion
Mn(IV)	manganic ion
$MnCO_3$	manganese carbonate
MnO_2	manganese dioxide
MnOOH	manganite
$MnSO_4$	manganese sulphate
Mo	molybdenum
N	nitrogen
N_2	nitrogen gas
Na	sodium
$Na_2B_4O_7$	Fertibor®
$Na_2B_8O_{13}.4H_2O$	Solubor®

$Na_2MoO_4.2H_2O$	sodium molybdate
NaOCl	sodium hypochlorite
NaOH	sodium hydroxide
NH_3	ammonia
NH_4^+	ammonium
NH_4HCO_3	ammonium bicarbonate
NH_4OAc	ammonium acetate
$(NH_4)_6Mo_7O_{24}.4H_2O$	ammonium molybdate
Ni	nickel
NO_2^-	nitrite
NO_3^-	nitrate
P	phosphorus
Pb	lead
P_2O_5	oxide of phosphorus
S	sulphur
Se	selenium
Si	silicon
SO_3^{2-}	sulphite
SO_4^{2-}	sulphate
Zn	zinc
$ZnFe_2O_4$	franklinite
$ZnNH_4PO_4$	zinc ammonium phosphate
$Zn(OH)^+$	zinc hydroxide
$ZnSO_4$	zinc sulphate
$ZnSO_4.7H_2O$	zinc sulphate heptahydrate

Abbreviations

APP	ammonium polyphosphate
BMP	best management practice
CEC	cation exchange capacity
cm	centimetre
CRF	controlled-release fertiliser
DAP	diammonium phosphate
DM	dry matter
DNA	deoxyribonucleic acid
DTPA	diethylene-triamine-pentaacetic acid
EDDHA	ethylenediamine di (ortho-hydroxyphenylacetic acid)
EDDHMA	ethylenediamine (ortho-hydroxy-P-methylphenylacetic) acid
$EDDH_4MA$	ethylenediamine-bis (2-hydroxy-4-methylphenyl) acetic acid
EDDHSA	ethylenediamine di (2-hydroxy-5-sulphophenyl acetate)

EDTA	ethylene-diamine-tetraacetic acid
h	hours
ha	hectare
HEDTA	hydroxyethyl-ethylenediamine triacetic acid
IPNS	integrated plant nutrition systems
M	mole
mm	millimetre
µg	micro gram
µM	micro molar
na	not available
NADH	nicotinamide adenine dinucleotide
NPK	fertiliser containing N, P and K
PDDHA	propylenediamine-di (ortho-hydroxyphenyl)acetate
PS	phytosiderophore
PTE	potentially toxic element
RDA	recommended dietary allowance
R,D&E	research, development and extension
RNA	ribonucleic acid
RNI	recommended nutrient intake
ROS	reactive oxygen species
SOD	superoxide dismutase
t	metric tonne
TPN	total parenteral nutrition
UAN	urea ammonium nitrate
UV	ultra violet
VCR	value:cost ratio
YEB	youngest emerged blade
YFEL	youngest fully expanded leaf blade
YOL	youngest open leaf
yr	year

Summary

Micronutrients are essential for the normal growth and health of plants, animals and humans. When soil or dietary supply are inadequate, defects in development arise and this can lead to poor growth and premature death. The World Health Organization, (WHO) in its 2000 World Health Report, identified the lack of dietary iron (Fe) and zinc (Zn) as serious global health risks. Micronutrient constraints in agriculture continue to be reported from around the world.

Micronutrients are of growing importance in crop and tree nutrition because of:

- increased demand from higher yielding crops and intensive cropping;
- continued expansion of cropping and industrial plantations onto marginal land with low inherent levels of micronutrients;
- increased use of high-analysis fertilisers containing low levels of micronutrients;
- decreased use of manures, composts and crop residues in some parts of the world;
- mining of micronutrient reserves in soils and;
- nutrient imbalances.

Micronutrients receive less attention in nutrient management and fertiliser research, development and extension (R,D&E) than macronutrients for the understandable reason that usage of micronutrients in crop production is lower. However, there is increasing evidence that the proportion of nutrient management R,D&E allocated to micronutrients is insufficient given their importance. Apart from the direct benefits for increased crop production, micronutrients increase the efficiency of use of macronutrient fertilisers. Awareness is growing that micronutrient levels in staple foods need to rise for the sake of improved human and animal health. Because of on-going community concerns about environmental contamination, in recent times, more research has been conducted on the pollution risks of micronutrients than on the benefits to be gained from their use in increasing food, feed, fibre and bioenergy production.

The publication places most emphasis on the micronutrients Zn, Fe and boron (B) since deficiencies of these micronutrients are most widespread and, globally, these elements have been subject to most research. However, examples are provided on the benefits of using the other essential micronutrients.

The micronutrient requirement by crops for normal growth and high yield is small compared to that of the macronutrients. Nevertheless, each of the micronutrients, B, copper (Cu), Fe, manganese (Mn), molybdenum (Mo), nickel (Ni) and Zn, meet the requirements for essentiality in plants and, despite the small amounts needed by crops to complete their life cycles, deficiencies of one or more of these elements frequently occur in agriculture, horticulture and forestry. Nickel is the most recent of the essential micronutrients for which field production responses have been confirmed.

Importance of micronutrients is a product of the impact per unit area and the area of impact. Impact of micronutrient deficiency in crop production is most commonly measured as loss of crop yield. However, for a range of crops, effects of micronutrients

on crop quality such as oil, protein or fibre content, absence of defects, and storage longevity are important for the price of agricultural products in markets. In other cases, low symbiotic nitrogen (N) fixation by legumes is the main impact of micronutrients in cropping systems. Low micronutrient levels in seed for planting are having large unrecognised impacts on the the costs of crop production and low levels in consumed foods are contributing to the high global levels of micronutrient deficiencies in humans.

Areas affected by micronutient deficiencies are not easy to estimate in part because of their dynamic change. Generally, approaches to defining the area of impact consider only the topsoil levels of micronutrients. However, there is emerging evidence that low sub-soil micronutrient status is an under-recognised constraint for which there are no reliable estimates of its extent.

Large opportunities exist through the development of Best Management Practices (BMPs) to increase crop production by applying micronutrients. Best Management Practices need to be tailored to local conditions. Micronutrients supplied in optimal forms and amounts and with optimal timing and placement, on soils with an inadequate supply, will generate benefits for producers and consumers providing other factors are not limiting. The principles governing optimal supply, methods of application and timing of application are discussed in detail. Provided these principles are adopted and there is a sound knowledge of input and outputs of micronutrients in farming systems, negative effects of micronutrients should be negligible or manageable. By considering the benefits of micronutrients in harvested plant products for human nutrition and in forages for animal nutrition, the benefits can be further extended beyond those based on yield alone.

Progressive increases in crop yields through improved varieties and agronomic advances are common in many farming systems. Unless micronutrient supply increases with increases in crop removal, deficiencies may emerge where they did not previously limit crop growth. Continued use of micronutrients, without regard to nutrient budgets, may lead over time to the accumulation of excessive levels that threaten food safety or environmental quality. Changes in agronomic practices and cultivars can also trigger the emergence of micronutrient deficiencies in farming systems where they did not previously exist. Best Management Practices for micronutrients in different farming systems need to continually evolve to allow for changes in the system, especially changes in inputs and outputs.

The future supply of micronutrients to agriculture and horticulture needs to recognise the increasing public scrutiny of food safety and environmental quality. Pro-active industry programmes are needed to ensure that the skills and knowledge of all individuals involved in the supply and distribution of micronutrients (and other nutrients) promote environmental stewardship, occupational health and safety, food safety and agricultural productivity. Industry schemes should aim to provide training and accreditation for these stakeholders in the fertiliser and soil ameliorant industry.

The on-going importance of micronutrients in agriculture necessitates comprehensive programmes to train human resources in each country. Clearly, the capacity to mount such training programmes is greater in developed countries than in most developing countries. Universities play a key role in developing a capacity for training, providing advice to farmers and conducting research that allows continual improvement of BMPs. This process is being greatly facilitated by the improved access to knowledge about micronutrients afforded by the internet. The rapid development of research capacity and outputs in the molecular biology of micronutrients in plants is generating important new understanding of the role of these elements in plants, and the potential to transform plants for improved micronutrient status. There remains the need to maintain and develop skills in the physiology of micronutrients in plants and crops, in the soil behaviour of micronutrients and in understanding the biogeochemical cycling of micronutrients in diverse agricultural, horticultural and forest (including plantation forests) systems.

This publication is dedicated to
Professor Jack Loneragan,
who inspired a generation of
scientists to work on micronutrients

1. Introduction

Micronutrients are of growing importance in crop and tree nutrition because of:
- increased demand from higher yielding crops and intensive cropping;
- continued expansion of cropping and forestry onto marginal land with low inherent levels of micronutrients;
- increased use of high-analysis fertilisers containing low levels of micronutrients;
- decreased use of manures, composts and crop residues in some parts of the world;
- mining of micronutrient reserves in soils; and
- nutrient imbalances (Fageria *et al.*, 2002).

The micronutrient requirements by crops for normal growth and high yield are small compared to those of the macronutrients (Epstein and Bloom, 2005). Hence, traditionally, emphasis in crop nutrition has been on nitrogen (N), phosphorus (P) and potassium (K). Nevertheless, each of the micronutrients listed in Table 1.1 meet the requirements for essentiality in plants and, despite the small amounts needed by plants to complete their life cycles, deficiencies of one or more of these elements frequently occurs in agriculture, horticulture and forestry.

Table 1.1. Essential micronutrients for higher plants and the relative amounts of each required for healthy plant growth (after Epstein and Bloom, 2005).

Element		Year essentiality first established; source	Typical concentrations in plants (mg/kg)	Relative number of atoms required for healthy plant growth[a]
Essential for all higher plants				
Boron	B	1923; Warington	20	2000
Chlorine	Cl	1954; Broyer *et al.*	100	3000
Copper	Cu	1931; Sommer	6	100
Iron	Fe	1860; Sachs	100	2000
Manganese	Mn	1922; McHargue	50	1000
Molybdenum	Mo	1939; Arnon and Stout	0.1	1
Nickel	Ni	1987; Brown *et al.*	0.05	1
Zinc	Zn	1926; Sommer and Lipman	20	300
Essential for some plants				
Cobalt	Co	1960; Reisenauer	0.1	2
Sodium	Na	1979; Brownell	10	400

[a] On the same relative scale, 1,000,000 atoms of nitrogen are required by plants.

The list of essential micronutrients for plants remains unchanged since 1987. This is fortunate since the task of managing micronutrient supply in a sustainable manner has proved challenging enough with the presently known essential micronutrients. An exciting recent development for micronutrients, is the report of nickel (Ni) deficiency in pecan in southeast USA (Wood *et al.*, 2004), the first confirmed field response to Ni since Brown, Welch and colleagues at Cornell University showed that Ni satisfies the criteria for essentiality in plants (Brown *et al.*, 1987).

Silicon (Si), which is presently not classified as an essential element, nevertheless remains the subject of significant research in the USA, Japan, and China (Datnoff *et al.*, 2001), and international symposia on Si were held in 1999 (Florida), 2002 (Japan) and 2005 (Brazil). Graham and Webb's (1991) review on the role of Si in disease suppression is still worth reading for a persuasive account of the unrecognised potential of Si to enhance crop production. Nevertheless, should Si be re-classified in the future as an essential element, the requirements in plants are sufficiently high that it would not be considered a micronutrient (Epstein and Bloom, 2005).

In recent times, there has been a new emphasis on micronutrients in the whole food cycle (Welch and Graham, 2005). In particular there has been a growth in research on micronutrient levels in staple grains because of their critical importance for the provision of micronutrient requirements in the human diet. Hence future emphasis on micronutrients may expand from their role in crop production, to their importance in the main staple foods in diets for sustaining human and animal health. When considering human and animal diets, the range of essential micronutrients is broader than for plants, and extends to a range of organic compounds such as Vitamin A (Welch and Graham, 2005). In the context of human and animal nutrition, micronutrient levels of arsenic (As), chromium (Cr), iodine (I), selenium (Se), and Si also need to be considered and, for ruminants, cobalt (Co) is essential (Van Campen, 1991). Fluoride (F), while not essential for animal life, is necessary for maintaining healthy bones and teeth. According to Nielsen (1984), lithium (Li) and vanadium (V) are probably essential but further study is required.

A larger number of micronutrients are recognised as essential for animals, but the criteria adopted for essentiality in animals is less demanding than that for plants (Asher, 1991; Graham and Webb, 1991; Epstein and Bloom, 2005). It is possible that some of the elements that are essential for animals will eventually be shown to be essential for plants. Strong grain responses to Se have recently been reported for *Astragulus* and *Arabidopsis* (Graham *et al.*, 2005). While Se has been recognised as essential in the diet of humans and animals since 1957 (Hartikainen, 2005), the present results still fall short of the critical evidence that Se is essential for plants. Conversely, boron (B) is essential for plants but not yet recognised as essential for animals and humans. However, research is building evidence that B is essential for animals and humans (Nielsen, 2002).

Importance of micronutrients

The importance of micronutrients in agriculture, horticulture and forestry can be defined as the product of:

- the magnitude of impacts per unit area, and
- the total area of impact.

Impact of micronutrient deficiency

The impact of micronutrient deficiencies on crop production is most commonly measured as loss of crop yield. However, a variety of other properties may be more important for the marketing of harvested plant products than yield, *per se*. For a range of crops, aspects of crop quality such as oil, protein or fibre content, are important for the price of agricultural products in markets. For forest products, tree form and wood quality may be as important as wood volume in determining the economic value of the harvest (Dell *et al.*, 2003). Hence the effects of B and copper (Cu) deficiencies on log form and wood quality are often the responses of prime interest for foresters. In other cases, physical defects of the harvested seed such as "hollow heart" in peanut, caused by B deficiency, may be important in markets (Morrill *et al.*, 1977). For mung bean, the viability and vigour of germinating seed, which can be impaired by low seed B (Bell *et al.*, 1989), may be a prime quality characteristic that determines market price in those parts of Asia favouring bean sprouts in the diet.

In a cropping system, the main impact of micronutrients may be on amounts of N fixed by legumes. Limitations of symbiotic N fixation decrease current crop production of legumes, but may have equally significant impacts on subsequent crops in the rotation due to lower residual soil N levels (Wood and Myers, 1987). Another aspect of impact is the effect of micronutrient concentrations in planting seed on the vigour of the next season's crop. This may impose hidden costs in the form of extra seed needed for crop establishment, and/or patchy, low yielding stands that under perform (Ascher-Ellis *et al.*, 2001), or reduced early crop vigour leading to lower yield potential (Rerkasem *et al.*, 1997). An emerging area of interest is the impact of micronutrient supply on grain quality for human and animal nutrition (Welch and Graham, 2005), but it is too early to assess the likely magnitude of these impacts on micronutrient use in agriculture and horticulture. For fertiliser retailers, the total value of micronutrient fertiliser sold is small compared to macronutrient fertilisers (Mortvedt, 1991). However, a major economic impact of micronutrients in a farming system is through the increased efficiency of macronutrient fertiliser use.

Comprehensive reviews of the impact of micronutrients on crop production are found in Vlek (1985), Mortvedt *et al.* (1991), Srivastava and Gupta (1996), Singh *et al.* (2001), Fageria *et al.* (2002) and Alloway (2008c). Major reviews for individual micronutrients are listed in Table 1.2.

Table 1.2. Major reviews for individual micronutrients.

Element	Authors and year
B	Gupta (1993), Dell *et al.* (1997), Goldbach *et al.* (2002), Xu *et al.* (2007)
Cu	Loneragan *et al.* (1981)
Mo	Gupta (1997a)
Mn	Graham *et al.* (1988)
Zn	Robson (1993), Alloway (2008a), Cakmak (2008a)
Fe	Biennial conferences since 1981 (Jones 1982; 1984; 1986; 1988; etc)[a]

[a] Proceedings of biennial conferences on Fe nutrition provide an on-going source of information about the impact of Fe deficiency in agriculture, horticulture and forestry.

Area of impact

Areas affected by micronutrient deficiencies, the second component of importance, are difficult to estimate. Generally, approaches to defining the area of impact consider only the topsoil content of micronutrients (Takkar *et al.*, 1989). However, there is emerging evidence that low sub-soil micronutrient status is an under-recognised constraint for which there are no reliable estimates of extent (Bell *et al.*, 2004). The work of Loneragan *et al.* (1987) and Loneragan (1988) suggests that the remobilisation of zinc (Zn) and manganese (Mn), respectively, within the root system is inadequate to support unrestricted root growth into media with low concentrations of these elements. In the absence of rigorous data on sub-soil micronutrient levels it is not possible to estimate the total area of cropped land affected by micronutrient deficiencies.

Most current reports on the area of impact record micronutrient status in the topsoil at a point in time, but fail to recognise dynamic changes in micronutrient status or land use over time. In Australia, for example, micronutrient deficiencies were first treated 30-50 years ago and, depending on the residual value of the added fertiliser, soils are often still considered adequate for crop yields 20-35 years after the initial applications (Cu- Gartrell, 1981, Brennan, 1994; Zn- Brennan, 1996; 2001). Hence areas of southern Australia that were once mapped as almost entirely deficient in Zn, Cu and molybdenum (Mo) (Donald and Prescott, 1975) are now generally adequate in topsoils for crop growth. Moreover, the adequate micronutrient status in topsoils is no guarantee that sub-soil levels are sufficient for unrestricted crop growth (Nable and Webb, 1993; Grewal *et al.*, 1997). For example, Nable and Webb (1993) showed that the sub-soil Zn may restrict water uptake and growth of wheat even when the topsoil Zn levels are adequate.

Changes in genotypes over time may also mean that an area once considered adequate in a micronutrient is now deficient. In Nepal, traditional lentil varieties tended to be B efficient and so, in the past, the prevalence of reported B deficiency for this crop was low. Improved varieties have higher yield potential but are also more prone to B deficiency (Kataki *et al.*, 2001). Another example is in south-western Australia, where about 200,000 ha of agricultural land have recently been converted from annual pasture and crop production to plantations of fast-growing *Eucalyptus globulus* (bluegum). Although soil residual values for Cu were adequate for farming following application of Cu fertilisers over the past three decades, Cu deficiency emerged as a serious problem leading to poor bole form and reduced tree growth (Dell *et al.*, 2003). This appears to be related to roots having poor access to micronutrients in surface soils during the dry season when most of the tree biomass is being laid down. Finally, as yield output from farming systems rises, areas that were previously adequate are now declining in micronutrient reserves in soils (Wong *et al.*, 2005), and hence deficiency is reported with increased frequency.

The challenge for the fertiliser manufacturers, distributors and agronomists is to find cost-effective means to continually update information on the locations and areas affected by micronutrient deficiencies. Wong *et al.* (2005) developed a flexible spatial modelling approach based on weight of evidence for mapping risk of B deficiency. This approach could be used to regularly update maps of micronutrient deficiencies.

Reviews of the global and regional areas affected by micronutrient deficiencies can be found in publications listed in Table 1.3.

Table 1.3. Key review papers outlining the areas affected by micronutrient deficiencies in different parts of the world.

Area	Source
Global	Sillanpäa (1982; 1990)
Global	Vlek (1985)
Global	Welch *et al.* (1991) ; Alloway (2008c)
Australia	Donald and Prescott (1975)
China	Liu (1992)
Mediterranean-type soils	Rashid and Ryan (2004)
Tropical Africa	Kang and Osiname (1985)
Tropical Asia	Katyal and Vlek (1985)
Tropical Latin America	Léon *et al.* (1985)
United Kingdom	McGrath and Loveland (1992)

Vose (1982) summarised the global risk of iron (Fe) deficiency. Iron deficiency is most common in arid and semi-arid regions and on alkaline soils developed on calcareous parent materials. Since the problem of Fe deficiency is difficult to correct and the residual value of Fe fertilisers is low, areas of Fe deficiency risk should have remained essentially unchanged since the review of Vose (1982), 25 years ago.

Shorrocks (1997) developed a global map of B deficient areas based on the location and prevalence of reported cases of B deficiency (Fig. 1.1). In general, these areas

Figure 1.1. Global distribution of B deficiency (adapted from Shorrocks, 1997).

coincide with regions of sandy soils and related geology coupled with strong leaching rainfall regimes, as well as areas with alkaline pH. Major regions of low-B soils include southern China; Thailand across to the Indo-Gangetic plain of India-Nepal, eastern and southern states of the USA. In some of the mapped low B areas, B fertiliser is regularly used so that the map does not reflect current deficiency, but rather potential deficiency in cases where B fertiliser is not used regularly.

Alloway (2008a) prepared a map of the regions of low-Zn soils based on the FAO World Soils maps of sandy, low-Zn soils and alkaline soils with low Zn availability (Fig. 1.2). Large areas of potential Zn deficiency occur in northern China, a vast region from India across the Middle East to the eastern Mediterranean; south and central Africa; central America; northeast Brazil; and southern Australia. This type of map is an indication of risk of Zn deficiency in the absence of Zn fertiliser use and without consideration of the local risk factors related to crop species grown or soil management technologies. In south-west Australia, widespread use of Zn fertiliser and its long residual value have largely corrected Zn deficiency and now only maintenance applications are needed. Similarly, in India, the widespread use of Zn fertiliser for rice-wheat rotations in the Indo-Gangetic Plain has decreased the prevalence of reported Zn deficiency (Nayyar *et al.*, 2001).

Global maps have not been prepared for Fe, Cu, Mn, Mo or other micronutrient deficiencies. However, some general principles can be used to identify regions where deficiencies will be common. Copper deficiency is commonly associated with peat (Welch *et al.*, 1991). Hence, the substantial areas of tropical peat in Malaysia, Indonesia and southern Thailand for example are prone to Cu deficiency (Ismunadji and Soepardi,

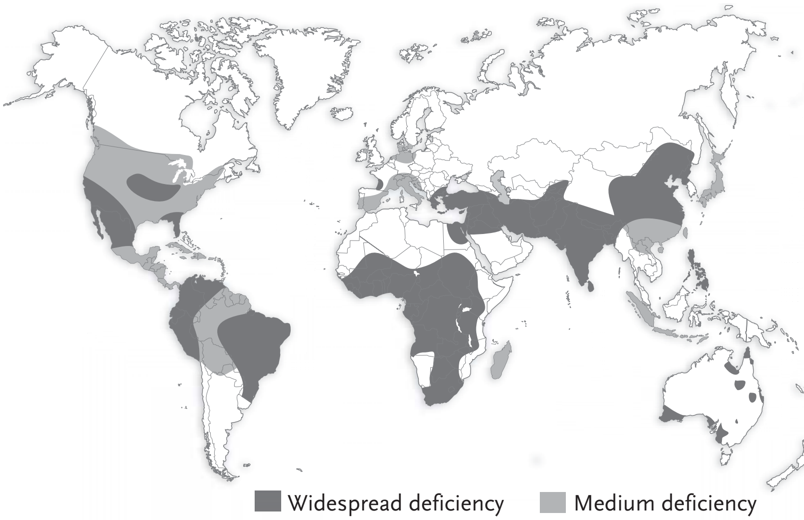


Figure 1.2. Zn deficiency in world crops: major areas of reported problems (adapted from Alloway, 2008a).

1984; Hashim, 1984). In addition, Cu deficiency is found on soils developed from a range of geologies, including sand, sandstone, acid igneous rocks and calcareous materials (Fageria *et al.*, 2002). It is not commonly found on clay soils and those developed from mafic rocks.

Manganese deficiency has a close correspondence with the regions of alkaline soils, and therefore overlaps in distribution with Fe and Zn deficiencies. However, the prevalence of Mn deficiencies is generally much less than for Fe or Zn. For example, in India 2 % of 90,000 soil samples were classed as deficient in Mn, 51 % were deficient in Zn and 10 % in Fe (Nayyar *et al.*, 2001). Moreover, Mn deficiency is also found on sandy acid soils where Fe deficiency is unexpected (Fageria *et al.*, 2002). Manganese deficiency also occurs on shallow peaty soils (Welch *et al.*, 1991).

Molybdenum deficiencies commonly occur on well-drained acid soils and on parent materials low in Mo (Gupta, 1997b). These conditions are met on soils developed on sedimentary rocks, basalts and granites. Extensive areas of low Mo soils occur east of the Mississippi River in the USA (Welch *et al.*, 1991), across much of the agricultural zone of southern Australia (Donald and Prescott, 1975), and in acid soils in India. Acid soils in the tropics also are commonly low in Mo and induce deficiencies in legumes (Johansen *et al.*, 1997).

Confirmed Ni deficiencies are at present very limited in occurrence (Wood *et al.*, 2004). Wood *et al.* (2004) reported that "mouse-ear" or "little-leaf" symptom has been noted in pecan for about 100 years, but has become increasingly common and more severe in recent years. The postulated causes have ranged from cold injury to viruses, nematodes and micronutrient deficiencies. Foliar sprays of Ni, using a variety of sources, have all corrected the problem whereas other treatments had failed to do so. The problem is most noticeable in replant orchard sites because of excessive accumulation of soil Zn (from decades of Zn applications). Thus, most of the Ni deficiency problems identified in pecan are induced by excessive usage of Zn. Wood *et al.* (2004) suggest there is considerable potential for Ni deficiencies in greenhouse and potted plant nurseries if there is over application of calcium (Ca), magnesium (Mg) and urea, and possibly nitrate. More recent results of Bai *et al.* (2006) indicate that the mouse-ear symptom in pecan is linked to the toxic accumulation of oxalic and lactic acids in the rapidly growing tips and margins of leaflets.

2. Micronutrients in soil

Biogeochemical cycling of micronutrients

For macronutrients there are abundant studies on biogeochemical cycling, but for micronutrients such reports are sparse or limited to particular pools and fluxes in the cycle (e.g. Alloway, 1995; Adriano, 2001; He *et al.*, 2005). A generalised schema for biogeochemical cycling on micronutrients is shown in Fig. 2.1. In this schema, the dissolved free and complexed forms of micronutrients are the mobile and readily available pool for uptake by plants, but usually a very small pool in the biogeochemical cycle. Minerals containing micronutrients are in dynamic equilibrium with the soil solution pool through dissolution and precipitation reactions. Iron and aluminium (Al) oxides, clay and humus also buffer the concentrations of micronutrient in the soil

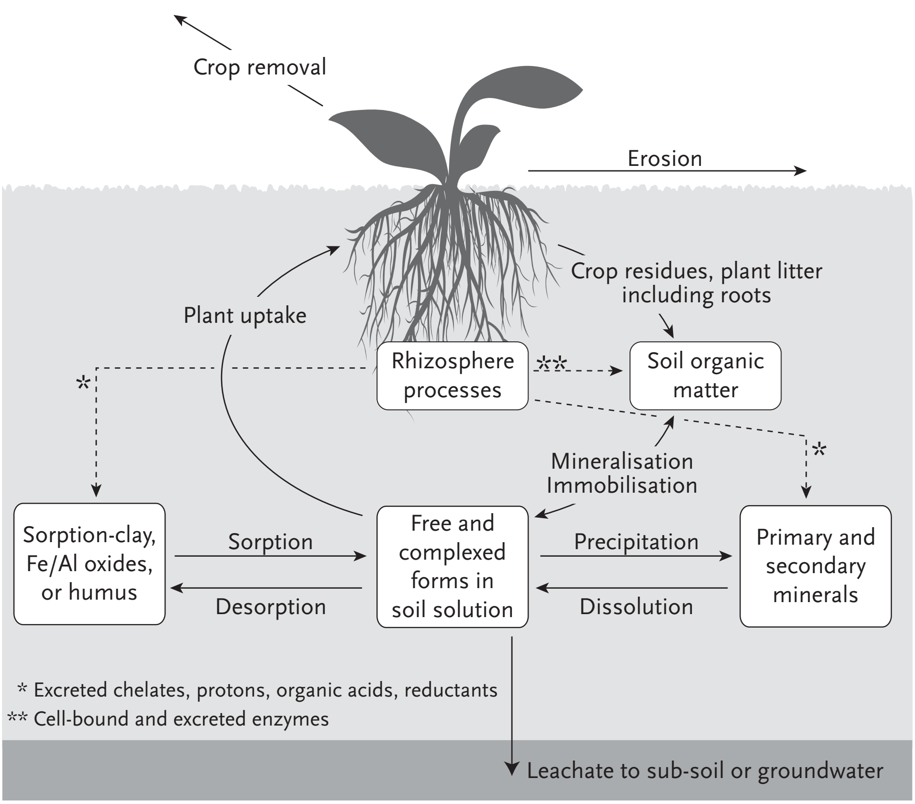


Figure 2.1. Biogeochemical cycling schema for micronutrients in the soil-plant system for aerobic soils.

solution pool through oxidation-reduction, adsorption-desorption and complexation reactions, many of which are affected by soil. The mineral and sorbed pools are generally the largest in the soil. Plant roots absorb micronutrients from the soil solution pool, but for most micronutrients, rhizosphere modification by roots increases the plant-available pool for uptake.

Crop removal may be a significant flux in the biogeochemical cycle under high yielding cropping systems such as the rice-wheat system of Asia. However, in low output agricultural systems, it is a minor flux (Fig. 2.1). The return of plant residues to the soil recycles micronutrients to the soil, while mineralisation releases them for either plant uptake or reactions with soil. Soluble organic compounds released by mineralisation may be significant in maintaining micronutrients in the soil solution by forming soluble chelates. Leaching and erosion are potential fluxes that remove micronutrients from the biogeochemical cycle, but few studies have attempted to quantify the amounts involved.

Fertiliser, anthropogenic pollutants and agricultural chemicals are additional inputs of micronutrients in biogeochemical cycles on agricultural land. While the generalised schema is a useful framework for the biogeochemical cycling of micronutrients, the importance of each pool and the fluxes connecting pools will vary among the micronutrients. The specific characteristics of the biogeochemical cycle for each element are highlighted hereafter.

Review papers concerning the specific biogeochemical behaviour of micronutrients in soils:

B	Goldberg (1997)	Cu	Baker and Senft (1995)
Fe	Lindsay (1991)	Mn	Gilkes and McKenzie (1988)
Mo	Reddy *et al.* (1997)	Zn	Barrow (1993)
Micronutrients in general	Barrow (1987); Lindsay (1991); Shuman (1991); Alloway (1995); Stevenson and Cole (1999); Adriano (2001) ; He *et al.* (2005) ; Alloway (2008c)		

Soil solution

Soil solution is the focal pool of micronutrients for plants. It is the fraction from which root absorption occurs, the fraction that participates in a range of chemical and biological reactions (Shuman, 1991) and also the fraction from which leaching or run-off losses can occur (He *et al.*, 2005; 2006). Soil solution concentrations of micronutrients are constantly changing in response to root uptake, changes in soil water content, mineralisation of organic matter, and sorption-desorption, complexation and redox reactions.

Few studies have attempted to extract soil solution micronutrients (Table 2.1). Soil solution B concentration ranges from < 1 to 10 μM although relatively few soils have been examined to date (Bell *et al.*, 2002). Boron is unique amongst the micronutrients in that it exists as a non-dissociated molecule under most soil pHs except as pH approaches the pKa (9.25 for boric acid) when the borate anion becomes more prevalent (Power and Woods, 1997). Molybdenum exists as an anion at all soil pHs above 4 (Lindsay, 1991), unlike the remaining micronutrient metals that exist in soil solution as cations or cationic complexes (Barrow, 1987).

The metallic micronutrients are often present in the soil solution in complexed form so that the free ion activity can be extremely low. Hodgson *et al.* (1966) reported that 76-99 % of Cu and 5-99 % of Zn in soil solutions were in organically bound or complexed form. More recently, Saeki *et al.* (2002) reported that 56 % of Cu and 20 % of Zn in soil solution was in the form of organic complexes. Both Cu and Zn form stable complexes with soluble fulvic acid (Harter, 1991).

Table 2.1. Micronutrient concentrations in soil solutions.

Micronutrient	Total (μM)	Free ion	Source
B [a]	1-10	-	Bell *et al.* (2002)
Cu [b]	0.001-1	-	Graham (1981)
Fe [c]	10-1000	10^{-11} to 10	Römheld and Marschner (1986)
Mn [d]	0.1-400	-	Gilmour (1977)
Zn [e]	0.01-1	-	Kochian (1991)

[a] From a small sample of Hawaiian soils and 20 soils of south-east Queensland.
[b] Up to 98 % of the total soil solution Cu may be organically complexed.
[c] pH dependent with the lower concentrations in the range corresponding to soil at pH 8. Total soil solution concentration exceeds the free ion Fe(III) with the difference due to soluble organic complexes (Kochian, 1991).
[d] Most of the soil solution Mn is present as the free Mn(II) ion. Mn concentrations in soil solution are very dependent on soil redox potential and pH with the high values in submerged or flooded soils and the low values in aerated, alkaline soils.
[e] Values cited for calcareous soils.

Lindsay (1991) noted that plants need in excess of 10^{-8} M Fe in solution to meet their requirements for growth, but that, at pH above 5.5-6, Fe oxides are unable to maintain such solution Fe concentrations. This invokes the need for Fe chelates or reduction of Fe(III) to Fe(II) in order to supply adequate concentrations of Fe for plant root uptake.

Soil minerals

Primary and secondary silicate minerals represent major pools of micronutrients in mineral soils, but they are in crystalline forms that are resistant to weathering. In the long term, these pools of micronutrients are an important determinant of plant-available levels in the soil (He *et al.*, 2005). Mafic volcanic rocks (rich in ferro-magnesium minerals- also known as basic rock), for example, typically contain higher levels of micronutrient metals than felsic (rich in feldspar and silica) volcanic rocks (Stevenson and Cole, 1999). Boron levels by contrast are higher in felsic volcanics such as granite, which hosts the B-silicate mineral, tourmaline (Table 2.2). Similarly, the claystones and siltstones contain higher micronutrient levels in general than sandy sediments.

Micronutrient contents in the parent rocks reflect the overall risk of deficiency in soils derived from the respective parent rocks.

Table 2.2. Abundance of micronutrients (mg/kg) in igneous and sedimentary rocks (Stevenson and Cole, 1999).

Element	Igneous		Sedimentary		
	Granite	Basalt	Limestone	Sandstone	Shale
B	15	5	20	35	100
Cu	10	100	4	30	45
Fe	27000	86000	3800	9800	4700
Mn	400	1500	1100	<100	850
Mo	2	1	0.4	0.2	2.6
Zn	40	100	20	6	95

Iron is a major constituent of many primary and secondary silicate minerals, however, it is the Fe oxides and oxyhydroxides that control Fe solubility in aerated soils (Lindsay, 1991). Similarly for Mn, Zn and Cu, oxide, sulphide and carbonate minerals control solubility rather than silicate minerals in the soil, even though the latter are an important pool of those micronutrients. Boron is an exception in that the alumino-silicate mineral, tourmaline is common in granitic rocks and is believed to be a major mineral source of plant-available B in soils. However, according to Lindsay (1991), it is still not clear whether tourmaline controls B solubility in soils.

Oxides and oxyhydroxides of Fe, Zn, Cu and Mn play a central role in the solubility of these micronutrients in soils (Lindsay, 1991), but the form and solubility of oxides and oxyhydroxides varies with the soil redox potential. In aerated soil, Fe is predominantly in the oxidised Fe(III) form and is associated with low solubility oxides and oxyhydroxides. Similarly, Mn in aerated soils is predominantly in Mn(IV) state, as a constituent of low solubility oxides.

Unlike Fe and Mn, Zn and Cu exist mostly in the divalent state in soils and hence do not undergo changes in redox state as a result of wetting and drying of soils. Similarly, B and Mo do not change redox state in soils hence their plant availability is not directly affected by wetting and drying of soils (Kirk, 2004).

Organic matter

Organically bound micronutrients are a relatively important pool for soil Cu, Mn and Zn (Stevenson, 1991). According to Shuman (1979), organically bound forms in 10 representative soils of south-east USA comprised 2-68 % of the Cu, 9.5-82 % of the Mn, and 0.2-14.3 % of the Zn. In 24 diverse soils, McLaren and Crawford (1973) found that 16-47 % of Cu was organically bound.

Organic matter has contrasting effects on micronutrient availability. Chelation of micronutrients with insoluble organic matter reduces availability (Stevenson and Cole, 1999). In peat soils, acute Cu deficiency is an expression of the strong complexation of Cu by insoluble humic acids. Manganese deficiencies are also common on peaty sands. Copper typically forms inner sphere bonds with two oxygen atoms in organic matter. For micronutrient metals, carboxyl and phenolic groups are the dominant retention sites on organic matter (Sparks, 2003), although amides and pyridine rings are also important for Cu complexation (Harter, 1991). However, chelates of soluble organic matter with micronutrients increase their plant availability (Stevenson and Cole, 1999). The low incidence of Cu deficiency on mineral soils has been attributed to the role of soluble organic chelates in the availability of Cu to plants.

Similarly, Yermiyahu *et al.* (2001) reported contradictory effects of organic matter on B availability. In their study, composted cattle manure was applied to sand at 1-10 % by weight. At low rates of B supply, compost application increased B concentration in the soil solution and B uptake by bell pepper plants. By contrast, increasing compost rate decreased B in the soil solution and B uptake. These results suggest that organic matter can be a source of B by mineralisation, and this is significant when soil B is low. However, compost also complexes B and decreases the soil solution B levels. These two opposing influences on plant available B levels may explain the apparently contradictory results that often surround the role of organic matter in B availability.

Precipitation-dissolution reactions

Iron and Mn forms in soils are more dominated by precipitation-dissolution reactions than for other micronutrients. Precipitation-dissolution reactions are particularly important controls on solubility of micronutrients in alkaline soils (He *et al.*, 2005).

Solubility of Fe in aerated soils is controlled by ferrihydrite ($Fe_2O_3.9H_2O$). Manganese solubility is affected strongly by pH and redox potential. In aerated soils, $MnCO_3$ is the most stable Mn mineral, but as redox potential drops MnOOH and MnO_2 begin to control Mn solubility in soils. $CuFe_2O_4$ and $ZnFe_2O_4$ are the respective Cu and Zn minerals in soils believed to control soil solution concentrations.

Redox reactions

The extent of redox reactions will vary among soils and over time in a particular soil as the oxygen supply varies. Low redox potential can occur in virtually any soil. Even well drained, aerated soils have microsites where lack of oxygen supply lowers redox potential. Soils in humid regions and irrigated soils suffer episodes of low redox potential following heavy rainfall events or irrigation. Other soils, such as irrigated rice soils or submerged wetland soils are anoxic for extended periods or semi-permanently. When oxygen in the soil or soil pores is exhausted, bacterial metabolism requires alternative electron acceptors, of which Fe(III) and Mn(IV) are most abundant in soils. Low redox potential results in reduction of Fe(III) to Fe(II) and Mn(IV) to Mn(II) (Kirk, 2004). In reduced soil, Fe and Mn solubility is greatly enhanced since most of the ferrous and manganous oxides are much more soluble than ferric or manganic compounds. Indeed, toxicity of Fe is common in some rice paddy soils as a result of the release of high concentrations of Fe(II) ions under low redox potential.

Other micronutrients are not prone to redox change under anoxia (Kirk, 2004). However, in submerged soils, sulphate reduction decreases availability of Fe, Mn and Zn due to the formation of insoluble sulphides. Generally, sulphides formed by reduction of sulphate precipitate as iron sulphide (FeS) since Fe is present in abundance in soils. However, Zn deficiency is commonly induced in submerged soils and ascribed to the formation of insoluble sulphides. Copper sulphides are generally soluble in anoxic submerged soils and hence Cu availability is not directly affected by redox potential.

Sorption-desorption reactions

Sorption reactions have a major effect on the plant available levels of B, Cu, Mo and Zn, but only a minor role in the availability of Fe and Mn to plants (Harter, 1991). Copper and Zn exhibit similarities in their sorption behaviour. Both exist in the divalent form at soil pH < 6, regardless of redox state. As pH rises, Cu and Zn hydrolyze in aqueous solutions to form $Cu(OH)^0_2$ and $Zn(OH)^+$, respectively.

Copper and Zn can be non-specifically adsorbed as outer sphere complexes on clay surfaces, sesquioxides and organic matter, but Cu has a greater tendency to form inner sphere complexes (Harter, 1991; Sparks, 2003). The sorption of both Cu and Zn is correlated with the clay content and CEC of soils, and tends to be higher when smectite-type clays are dominant in the soil than with kaolinite or sesquioxides.

Increases in soil pH increase sorption of Zn strongly, and Cu to a lesser extent, indicating that sorption on variable charge surfaces is an important process affecting plant availability in soils (Barrow, 1987). Greater Zn and Cu sorption on surfaces is reported for the amorphous forms of hydrous Fe, Mn and Al oxides, reflecting their greater surface area. Copper sorption on the surfaces of Fe oxides, haematite and goethite increase strongly as pH increases above 4.5 (McKenzie, 1980). With Zn, sorption on the Fe oxides increases most strongly as pH increases above 5.5.

Mo sorption in soils is strongly dependent on the variable charge surfaces (Barrow, 1987). Like phosphate, the molybdate oxyanion is more strongly sorbed as pH declines. Hence in acid soils, low Mo availability is associated with its adsorption.

Boron sorption reactions are attributed to inner sphere complexation by Goldberg (1997), and to sorption of $B(OH_4)^-$ on variable charge surfaces by Barrow (1989). However, whatever the mechanism, B sorption on Al and Fe oxides, calcite, humic acid and alumino-silicate clays increases with pH and peaks in the pH range 8-10 in soil (Goldberg, 1997).

Crop removal

Small amounts of micronutrients are removed in harvested parts of crop and pasture species. Relative to the rates of addition of fertilisers, removal in a single crop is usually low and ensures extended residual value of micronutrient fertilisers in many cases. Brennan (2005) calculated that only 7 % of the Zn applied at the rate of 3 kg Zn/ha had been removed in harvested grain over the subsequent 14 years. Relative annual uptake of Cu by wheat crops from an initial application of 1.38 kg/ha was estimated to be 2-3 % per annum (Brennan, 2006). However, in intensive high yield cropping systems such as rice-wheat rotations or horticultural crop production, the removal of micronutrients in harvested crop products in a single year may account for 0.50 kg Zn/ha (Table 2.3), which necessitates either higher rates of micronutrients added in fertiliser or more frequent applications to maintain adequate supply for crop production. Similarly, in plantation forestry, high uptake rates of micronutrients and sequestration of them in bark and wood may necessitate higher rates of application than was required in previous land use systems on the same soil (Dell *et al.*, 2003). Therefore, it is important to account for crop removal and to determine, for a particular cropping system, the frequency with which repeat applications are needed.

Tables 2.3 and 2.4 present representative values for crop removal of micronutrients drawn from a number of sources and species. Clearly the amounts removed are dependent on yield, and values should be adjusted when expected yields differ from those reported in Tables 2.3 and 2.4. However, a doubling of yield will not necessarily double the removal of micronutrients. Many cropping systems involve sequences of crops with two or more crops per year and, under these circumstances, the annual removal is likely to be greater than that for a single crop annually (Table 2.4).

Table 2.3. Removal of micronutrients in harvested plant parts for a range of crop species (g/ha) (Price, 2006, unless otherwise mentioned). Ni uptake is not well enough studied to assign values for removal in harvested crops but levels are likely to be similar to Mo.

Crop type	Yield (t/ha)	B	Cu	Fe	Mn	Mo	Zn
Legume (peanut)[a]	2 (as pods)	154	16	1500	128	4	48
Cotton	2	-	20	158	50	-	98
Leafy vegetable (spinach)	50 (fresh leaves)	195	24	1200	175	25	100
Sugarcane	92 (stalks)	-	58	3404	1472	-	258
Fruit tree (orange)	Fresh fruit	157	34	168	45	-	78
Nut tree (pecan)	1.2	12	10	34	95	2	35

[a] From Singh *et al.* (2004), based on a crop yielding 2 t pods/ha and 3.6 t shoot biomass/ha.

Table 2.4. Micronutrient uptake (g/ha) by rice and wheat in a rice-wheat rotation averaged over three years in India under nil, low and high fertiliser rates (Gupta and Mehla, 1993).

Fertiliser rate	Biomass (t/ha/crop)		Rice				Wheat			
	Rice	Wheat	Zn	Cu	Mn	Fe	Zn	Cu	Mn	Fe
Nil	6.5	4.1	120	90	350	1680	70	30	110	700
Low	8.8	7.5	170	130	570	2510	120	50	210	1300
High	14.5	12.4	300	220	970	4060	200	90	330	2230

Erosion

Specific studies on erosion losses of micronutrients have not been sighted, hence most of our understanding is based on the application of principles and anecdotal information. When micronutient metals are concentrated close to the soil surface, erosion losses of soil could have a disproportionate effect on losses of micronutrients. For example, if 1 cm of soil was eroded and it contained 1 mg Zn/kg, this equates to a loss of 0.13 kg Zn/ha. Minimum tillage systems and broadcasting miconutrients will tend to concentrate micronutrients close to the soil's surface, and hence increase the risk of loss in the case of erosion events. Sub-soil Zn is commonly lower than in topsoils (Brennan *et al.*, 1993). Therefore, loss of topsoil commonly results in Zn deficiency on the exposed sub-soils (Fageria *et al.*, 2002). Copper which is strongly associated with organic matter would, like N, be lost disproportionately when surface erosion removes the humus-rich layers. According to McBride (1981), the plant available forms of Cu tend to be concentrated towards the soil surface. The micronutrients that are more strongly associated with the mineral soil components would tend to be depleted when erosion selectively removes mineral sediments from the soil.

Leaching

At recommended rates of application, B is the only micronutrient for which leaching is likely to be a significant flux in the biogeochemical cycle in aerobic soils. For the micronutrient metals, the low rates applied and the rapid soil reactions in aerated soils mean that very low levels of ions exist in soil solution and the risk of leaching is low.

Boron appears to leach readily from surface soils especially in sandy textured soils with neutral to acidic pH, but much less so in heavy clay soils (Saarela, 1985). Three years after it was applied to soils in Finland, less than 25-40 % of the B was recovered in the hot water soluble B fraction from the surface 25 cm layer of sandy and loamy soils, whereas all of the added B was recovered in an heavy clay soil. In the sandy and loamy soils, significant B accumulated in the 25-50 cm layer. However, even in soils with 200-400 g clay/kg, B leaching was reported by Parker and Gardner (1982) and Wild and Mazaheri (1979). Pinyerd *et al.* (1984) found a linear relationship between cumulative rainfall and B leaching from the ploughed layer (0-25 cm) of a loamy sand with low organic matter levels. However, whilst leaching resulted in soil B levels in the 0-25 cm layer declining after 1 year to the same level as in the unfertilised soil, all the fertiliser B added (up to 10 kg B/ha) was recovered in the B horizon suggesting that it had not been lost from the rooting zone. Similarly, in the studies of Baker and Mortenson (1966), extractable B levels in soils treated with B fertiliser remained higher than untreated soils, 5 years after the application.

In three contrasting soils of south-east China, leaching of B below 40 cm depth generally was not evident despite the fact that sites experienced 1500-1700 mm annual rainfall, most of it concentrated in 8 months, and despite the fact that the soils contained 200-260 g clay/kg in the surface layers (Wang *et al.*, 1997). Wang *et al.* (1997) showed there was more evidence of downwards movement of B when 3.3 kg B/ha was applied than with 1.65 kg B/ha, but there was no measurable increase in extractable soil B below 40 cm depth in either case. Repeat application of 3.3 kg B/ha for two successive years increased extractable B by 0.1 mg B/kg below 60 cm depth in the sandy loam alluvial soil, but even the application of 3.3 kg B/ha for the third successive year did not increase extractable B below 60 cm in the red soil. Boron leaching below 20 cm from borax applications accounted for 0-37 % of 9.9 kg B/ha applied. However, Wang *et al.* (1997) presented evidence that most of the B leached below the 0-20 cm layer accumulated in the 20-40 and 40-60 cm layers where it probably remained accessible to the roots of oilseed rape. Thus, whilst fertiliser B was probably not lost from the root zone by leaching, redistribution of B in the 0-40 or 0-60 cm layers by leaching dilutes the added B in a larger volume of soil. The accumulation of amorphous Fe oxyhydroxides in soils, which are alternately flooded and drained, may decrease B leaching (Jin *et al.*, 1987; Tsadilas *et al.*, 1994) and may account for the limited evidence of B leaching from the B fertiliser additions reported by Wang *et al.* (1997; 1999).

A number of studies have examined Zn leaching and concluded that little Zn leaching occurs under most conditions at recommended rates of Zn fertiliser application. Brennan and McGrath (1988) found that most of the applied Zn was recovered within 3-5 cm of its placement on a very sandy soil (4 % clay), after 1438 mm of cumulative rainfall that fell mostly over a 5-month period. There was no evidence of Zn movement more than 6 cm depth from an initial application of 0.75 kg Zn/ha as sulphate salt. When the Zn rate was increased tenfold to 22.4 kg/ha or greater, 12 % of the added Zn was recovered in the 5-15 cm soil layer. Therefore, on a permeable sandy soil, only at rates of application more than 10 times higher than recommended was there clear evidence of Zn leaching but, even so, the depth of penetration of Zn in the leaching front was < 15 cm. Hence Zn leaching is unlikely except under circumstances such as described by He *et al.* (2006) where high Zn loadings have occurred on acid sandy soils from past use of fungicides.

For Mo, the extent of leaching depends on soil Mo sorption. On alkaline sands, Jones and Belling (1967) reported 60-95 % of added Mo was leached below 16 cm depth with only 444 mm of rainfall equivalent. In acid soils where Mo availability is lower due to Mo sorption, the extent of Mo leaching is variable. On an acid sand (pH 5.2-5.7), Jones and Belling (1967) found 50 % of the Mo added was leached from 16 cm columns by 450 mm of water. By contrast, Riley *et al.* (1987), found that only 10 % of Mo leached from two grey sands (< 1 % clay) and negligible Mo leached from three acid sands (pH 5-5.4; 5-14 % clay) when applied at the rate of 40 g/ha and 500 mm of water was applied. Hence, the cases where Mo leaching was reported involve higher rates of application than normally applied to correct deficiency. Since Mo deficiency is not encountered on alkaline soils, fertiliser application on them is unlikely, and Mo leaching would only be from native soil Mo or Mo supplied in other soil additives.

Copper is remarkably immobile in soil and hence unlikely to leach. Indeed, the immobility of Cu is such that fertiliser Cu usually has to be well mixed in the rooting zone to achieve most efficient uptake by crops (Gartrell, 1981). However, in soils that have accumulated high levels of micronutrients like Cu and Zn from agricultural chemical additions, leaching of these micronutrients can be significant and have impacts on downstream water quality (He *et al.*, 2006).

Iron and Mn also are unlikely to leach in aerobic soils. However, in anaerobic soils, such as those used for paddy rice, Fe and Mn are present at high concentrations in the soil solution as soluble Fe(II) and Mn(II) (Kirk, 2004) and hence susceptible to leaching.

Modelling biogeochemical cycling

Developing a complex biogeochemical cycle for each micronutrient in a range of cropping systems would involve considerable labour-intensive research. Some progress has been made for micronutrients, but mostly in the context of heavy metal toxicity (Adriano, 2001). The processes involved in metal toxicity may not be relevant to biogeochemical cycling of micronutrients at deficient to adequate levels in agricultural systems. Brennan (2005) argued that for micronutrients, a simpler nutrient budget approach would usually be sufficient to account for the major pools and fluxes in agro-ecosystems (see Chapter 7). In a micronutrient budget, the key inputs are fertiliser and impurities associated with agricultural chemicals, and crop removal is the key output. However, there is scope for a greater understanding of biogeochemical cycling of micronutrients in agriculture, horticulture and forestry.

One of the few detailed studies of B cycling in crop production is that on Malaysian oil palm by Goh *et al.* (2007). Oil palm plants were treated with $Na_2B_4O_7$ (Fertibor®) at 3 kg B/ha/yr and sampled destructively at 20, 37, 46, 58, 71 and 81 months after field planting. In addition, 16 year-old plants were sampled to represent mature trees. Annual B uptake increased from 19 g B/ha in year 1 to 286 g B/ha in year 6, and thereafter declined to 185 g B/ha in year 12 (Fig. 2.2). The standing oil palm at 16 years old accumulated about 570 g B/ha in its vegetative dry matter and would continue to accumulate up to 750 g B/ha if left until 25 years old before replanting. The recycling of biomass from the mature oil palm plants using a zero-burn approach at the time of replanting should supply most of the B requirements for the next 4 years of growth, provided leaching losses were not excessive and the newly established roots were efficient in B uptake. The B requirement was mainly for canopy development and production of fresh fruit bunches, which remove 52 g B/ha/yr. The B demand for root growth peaked at 4 years before other plant components, suggesting substantial plant investment in early root growth. The stem reached peak B content after 5 years, the canopy after 7 years, and fresh fruit bunches 9 years after planting. Goh *et al.* (2007) suggested that in mature plantations, which have reduced annual B requirements, the pruned leaves if stacked around the base of plants would supply about 70 g B/ha/yr and meet most of the B requirements for new stem and root growth each year.

Soil classification and micronutrient deficiencies

Fageria *et al.* (2002) proposed an association between major soil groups (US Soil Taxonomy and World Reference Base) and potential micronutrient deficiencies, compiled from various sources (Table 2.5). A wide range of Soil Orders express micronutrient deficiencies, but Alfisol, Entisol (Psamments), Mollisol, Spodosol and

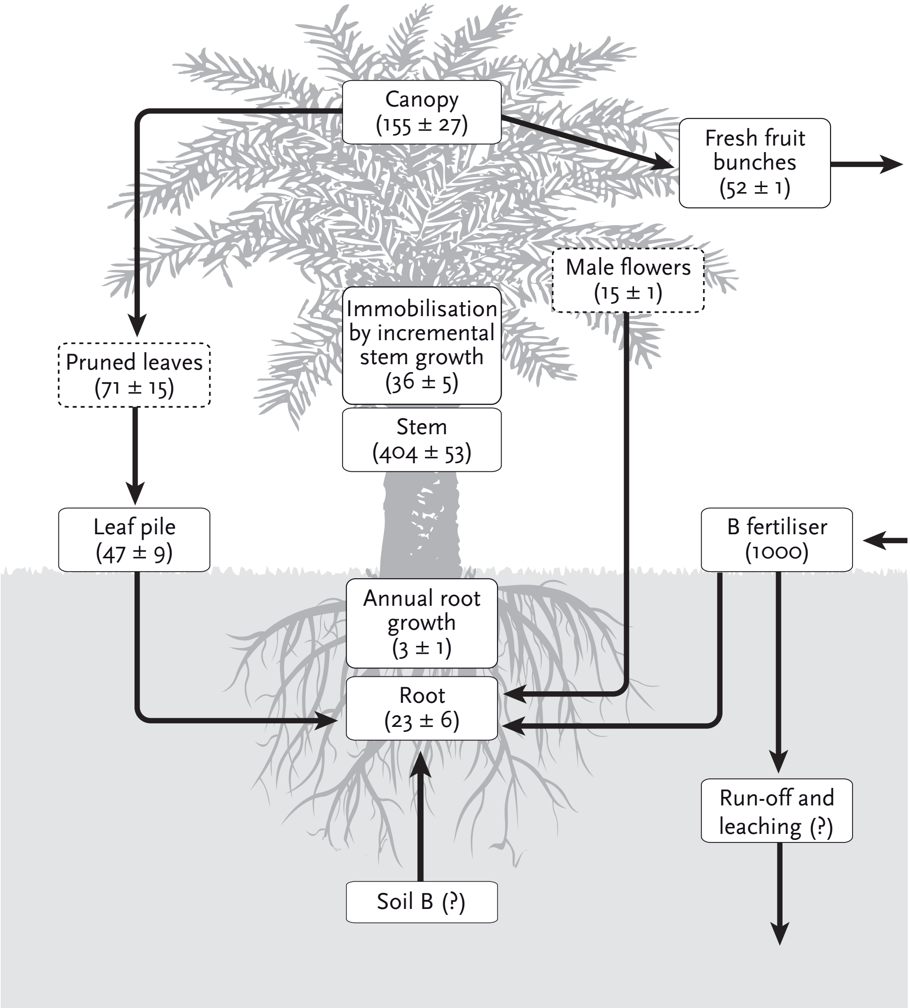


Figure 2.2. Boron cycling in mature oil palm plantations and within plants (Goh *et al.*, 2007). Values in boxes represent mean ± standard errors in g/ha/yr. Question marks indicate unknown values. Dotted boxes represent B recycled to the oil palm.

Ultisol Soil Orders seem to represent greatest risk of multiple deficiencies. By contrast, Cu deficiency is the single most likely micronutrient deficiency on Histosols. However, each of the major soil groups or Soil Orders is broad, representing a diverse range of soil properties, and hence Table 2.5 should serve only as a general guide to the risk of deficiency. Shorrocks (1997) summarises the Soil Orders in the regions with prevalent B deficiency: they belong to the Ultisol, Lithic Inceptisol, Lithic Fluvent, Alfisol, Psamment, Oxisol, Spodosol and Andept. Surprisingly, only the Andept appear in the list of Fageria *et al.* (2002).

Table 2.5. Relationships between major soil groups (Soil Orders in US Soil Taxonomy and Soil Groups in World Reference Base-WRB) and potential micronutrient deficiencies (Fageria *et al.*,2002, from various studies).

Soil Order (Soil Taxonomy[1])	Soil Group (WRB[2])	Element
Andosols (Andepts)	Andosol	B, Mo
Ultisols	Acrisol	Most
Spodosols (Podsols)	Podsol	Most
Oxisols	Ferralsol	Mo
Histosols	Histosol	Cu
Entisols (Psamments)	Arenosol	Cu, Fe, Mn, Zn
Mollisols (Aqu), Inceptisols, Entisols (poorly drained)	Gleysol	Mn
Mollisols (Borrols)	Chernozem	Fe, Mn, Zn
Mollisols (Ustolls)	Kastanozem	Cu, Mn, Zn
Mollisols (Rendolls) (shallow)	Rendzina	Fe, Mn, Zn
Vertisols	Vertisol	Fe
Aridisols	Xerosol	Fe, Zn
Alfisols/arid Entisols	Yermosol	Co, Fe, Zn
Alfisols/Ultisols (Albic) (poorly drained)	Planosol	Most
Alfisols/Aridisols/Mollisols (Natric)	Solenetz	Cu, Fe, Mn, Zn

[1] Soil Survey Staff, 1998.
[2] World Reference Base; ISSS-ISRIC-FAO, 1998.

Evaluation of the status of micronutrients in soils

Fractionation of micronutrient content in soils can be useful especially when related to plant uptake, as it helps to identify the plant available pools and the main pools of micronutrients in the soil, as well as the fate of those supplied by fertiliser, or recycled from crop residues (Shuman, 1991). As discussed above, micronutrients occur in soils in a variety of forms, with differing reactivity and plant availability, hence the fractions removed chemically are not discrete pools. In particular, it is difficult to extract the organic matter fraction without also removing oxide-bound and sulphide forms of micronutrients (Shuman, 1991). While there are variations among various published schemes, most attempt to separate the forms identified by Shuman (1991):

- water-soluble,
- exchangeable,

- specifically adsorbed,
- organically bound,
- bound to Fe and Al oxides,
- carbonate,
- sulphide, and
- residual.

Some fractionation schemes segregate the Fe and Al oxides into crystalline *vs* amorphous forms, while others attempt to selectively extract Mn oxides.

Shuman (1991) reviews the research on selective extraction of micronutrients. Depending on the purpose of the fractionation, one or more of these fractions may be omitted from the analysis and choices can be made among extractants for a particular fraction. The organic matter fraction of micronutrients is often the most problematic with none of the options being able to extract organically bound fractions exclusively without extraction of portions of another fraction. According to Shuman (1991), NaOCl offers the best compromise between extracting most micronutrients from organic matter and least from other fractions.

Most micronutrient metals are found in oxide and residual forms, which are regarded as having low plant availability (Shuman, 1991). The water soluble and exchangeable fractions are most available to plants. Copper associated with organic matter is tightly bound, while for Mn, Fe and Zn, this fraction is moderately plant available. While the Mn, Fe and Al oxide forms of Zn and Cu are not readily available, for Fe and Mn the solubility of the oxides depends on their degree of crystalinity, redox potential and pH.

Various B fractionation procedures have been developed. Jin *et al.* (1987) and Tsadilas *et al.* (1994) extracted the following fractions of soil B: soil solution B; non-specifically adsorbed B; specifically adsorbed B; B occluded with Mn oxyhydroxides; B associated with amorphous Al and Fe oxyhydroxides; B in crystalline Al and Fe oxyhydroxides; and B in silicate minerals. A modified fractionation scheme for B was proposed by Hou *et al.* (1996) and Siba *et al.* (2002): they involve oxalate extraction alone for B associated with oxides, and include a NaOH extraction for organically bound B. The importance of accounting for B bound with organic matter remains unclear (Xu *et al.* 2001). Jin *et al.* (1987) found that the B concentration in corn tissue correlated positively with water-soluble B, but also with non-specifically adsorbed B, specifically adsorbed B, and Mn oxyhydroxide-occluded B. Tsadilas *et al.* (1994) showed that B content in olive tree leaves was well correlated with amorphous Fe-Al oxyhydroxide-occluded B, specifically adsorbed B, and Mn oxyhydroxide-occluded B besides water-soluble B. By contrast, in barley leaves, B content was correlated with non-specifically adsorbed B as well as amorphous Fe-Al oxyhydroxide-occluded B, specifically adsorbed B, and water-soluble B, but not with Mn oxyhydroxide-occluded B (Tsadilas *et al.*, 1994). Xu *et al.* (2001) found that the forms of B in Chinese soils were distinctly different from those in soils of south-east USA and Greece (Jin *et al.*, 1987; Tsadilas *et al.*, 1994). In all studies, only 1-3 % of total B was associated with non-specifically adsorbed B and specifically adsorbed B, the forms most readily available to plants.

The above schemes for fractionating soil micronutrients are usually applied to the bulk soil. However, the availability of micronutrient metals in the root rhizosphere can be vastly different to that in the bulk soil due to effects of organic chelates, protons, reductants, and enzymes excreted by roots (Marschner, 1995). Therefore, there is some doubt about the value of fractionation data from bulk soils for predicting plant availability in species and cultivars that induce major changes in the rhizosphere to overcome the low levels of plant-available micronutrients in the bulk soil. Wang *et al.* (2002) showed that rhizosphere forms of micronutrients were better correlated with plant uptake when analysed on fresh, moist soil samples rather than on air-dried samples. Air drying rhizosphere soil substantially increased the levels of the readily available fractions of the micronutrient metals (cadmium (Cd), chromium (Cr), Cu, Ni, lead (Pb) and Zn).

In flooded soils, a different set of rhizosphere processes operate to increase plant availability of Zn, Mn and Fe (Kirk, 2004). Radial oxygen loss from the aerenchyma of roots causes oxidation of Fe(II) in the rhizosphere, which lowers pH. The acidification of the rice rhizosphere is responsible for increased Zn uptake by increasing available forms of Zn and by lowering levels of HCO_3^-, which impairs Zn uptake (Kirk, 2004). Sulphides oxidise in the rhizosphere and through this mechanism also, availablity of Zn is increased.

Forms and availability in soils

While it is recognised that water-soluble and exchangeable forms of micronutrients are the pools most readily accessed by plant roots, dilute salt and dilute acids that extract at pH and ionic strength comparable to plant roots usually remove too little of the micronutrients for easy measurement, and hence have been replaced as soil test extractants by chelating agents (Sims and Johnson, 1991). For Fe, Mn, Zn and Cu, the most commonly used extractant to estimate the plant available fraction is DTPA (Lindsay and Norvell, 1978). Variations on this extraction include the DTPA-ammonium bicarbonate solution (Brennan *et al.*, 1993). Also in common use is EDTA, and the Mehlich 3 extractant, which includes EDTA (Sims and Johnson, 1991). By lowering the activity of the micronutrient metal in the soil solution, chelates release labile soil pools into solution. Hence the chelates estimate the amount of micronutient metals in the soil solution as well as soil bound pools that are in dynamic equilibrium with the soil solution (Sims and Johnson, 1991).

The original DTPA extraction procedure was developed for alkaline soils and involved control of extraction pH by buffering at pH 7.3 and control of ionic strength to avoid dissolution of carbonates in the soil. However, this extractant is now commonly used on acid soils as well. On acid soils, DTPA will extract at varied pH depending on the inital soil pH and buffering capacity. Critical values for Zn vary with soil properties. Critical Zn concentrations varied with DTPA from 0.13 to 0.55 mg/kg depending on soil pH, clay and $CaCO_3$ content (Brennan and Gartrell, 1990). Apart from DTPA, Zn soil testing is carried out with 0.05 M HCl, 1 M NH_4OAc and the DTPA-ammonium bicarbonate extractants. Critical Zn values in soils using the DTPA extractant are 0.5-1 mg/kg (Sims and Johnson, 1991).

Several reviews have cast doubt on the value of DTPA or that of any other presently used extractant to predict Mn deficiency (Reisenauer, 1988 ; Uren, 1999). The latter authors argue that Mn availability in the soil is too dynamic, and responsive to changes in pH, soil water potential, soil temperature, root exudates and microbial activity to expect reliable prediction of Mn availability to a crop species during a growing season. By contrast, Sims and Johnson (1991) report on several cases where soil tests have been useful predictors of Mn response, especially when supplemented by information on other soil properties like pH, organic matter, $CaCO_3$ levels and texture. While DTPA is the most common extractant used for estimating soil Mn availability, a number of acid extractants (0.05 M HCl, 1 M NH_4OAc) have been used to asssess Mn status of soils. For prediction of Mn deficiency, critical values range from 1 to 5 mg Mn/kg.

Plant availability of Fe is also difficult to assess accurately with a soil test (McFarlane, 1999). Soil pH, redox potential, moisture content, bicarbonate concentration and temperature all alter Fe availability. In addition, major differences among plant species and among cultivars of the same species in acquisition of Fe from soil raise questions about the accuracy of soil Fe tests. Often, recommendations for Fe treatment are based on the sensitivity of a crop species and the soil type alone without reference to a soil test (Sims and Johnson, 1991). Of the soil tests commonly used, DTPA and DTPA-ammonium bicarbonate are most common and 4.5-5 mg Fe/kg is a typical critical value (Sims and Johnson, 1991).

Soil tests for predicting Cu deficiency are most reliable when calibrated and used for a restricted range of soils (Brennan and Best, 1999). Extraction using chelating agents such as EDTA or DTPA have been most effective, but inclusion of other soil properties, such as pH, CEC, organic matter and Fe, Al oxides and clay content in the calibration relationship may improve the accuracy of predictions. Viets and Lindsay (1973) pointed out that Cu soil tests remove 20-80 times more Cu during soil extraction than plants remove in the growing season. This emphasises the empirical nature of the relationship between soil test and crop uptake. The soil test can only be effective in predicting deficiency under conditions comparable to those for which the empirical relationship was derived. There is still a limited range of published information on the critical values for predicting Cu deficiency by soil analysis (Brennan and Best, 1999).

Plant-available B is usually extracted by hot water, or hot 0.01 M $CaCl_2$ (Bell, 1997; 1999). Several studies have sought to identify better soil B test procedures than hot $CaCl_2$ extraction, which has become a standard for most laboratories (Jahiruddin and Cresser, 1997; Datta *et al.*, 1998; Ratto de Miguez *et al.*, 1999; Tsadilas and Chartzoulakis, 1999; Matsi *et al.*, 2000) but, so far, there is no convincing evidence that alternatives are superior to hot $CaCl_2$ for prediction of B deficiency (Bell *et al.*, 2002).

Whereas Gupta *et al.* (1985) suggested the hot water extracted B from soluble inorganic, organic and adsorbed inorganic pools, recent attempts to fractionate soil B and to relate plant uptake to supply from specific fractions (Jin *et al.*, 1987; Tsadilas *et al.*, 1994) provide more compelling evidence about the plant available B pools. Such studies establish a sound basis for soil B testing, which has been previously lacking. In 20 soils from Greece, hot water B was correlated with all B fractions extracted apart from the Mn oxyhydroxide fraction (Tsadilas *et al.*, 1994). A multivariate regression model suggested that plant B uptake was best explained by variation in the cold water soluble B, mannitol extractable B and $NH_2OH.HCl$ extractable B. These fractions correspond approximately to the soil solution, specifically adsorbed B and B occluded in Mn oxyhydroxide fractions, respectively. That hot water seemed to extract B from the first two fractions but not the third suggests a possible reason why it may fail on some soils to predict plant response to B. Moreover, the fact that B uptake by olive trees was correlated with B in the Mn oxyhydroxide fraction, but that by barley was not, suggests a possible reason why hot water soluble B may be better correlated with B response in some species than others.

Ratto de Miguez *et al.* (1999) report that 0.02 M $CaCl_2$-extractable B was correlated with organic matter levels in soils of the Argentine Pampas. Datta *et al.* (1998) also found that extractable B was correlated with organic matter levels in acid soils of West Bengal, and Zerrari *et al.* (1999) found a similar positive relationship for Moroccan soils. Zerrari *et al.* (1999) conducted a fractionation study of soil B on Moroccan soils. Boron uptake by barley on these soils exceeded amounts of B extracted in the easily soluble (0.01 M $CaCl_2$ extractable) and specifically adsorbed fractions (0.05 M KH_2PO_4 extractable). It was concluded that organic matter-bound B and oxide-bound B were significant additional pools for plant uptake. This contrasts with studies of a range of soils from eastern China where there was no correlation between organic matter levels in the soils and any of the soil B fractions extracted, or with hot water soluble B (Xu *et al.*, 2001). However, Xu *et al.* (2001) did not examine the correlation between soil B fractions and plant response. Nevertheless, the role of organic matter in B availability to plants remains poorly understood.

There is limited understanding of the different pools of Mo in the soil and this hampers the development of effective soil tests for predicting Mo deficiency (Sims and Eizazi, 1997). In any case, the very low levels of Mo found in soils render accurate soil Mo tests difficult. In addition, seed Mo reserves can be sufficient to supply the requirements for the entire life cycle of a crop, so that sowing high Mo seed on a low Mo soil may prevent deficiency (Bell *et al.*, 1990b). Ammonium oxalate (pH 3.3) is the most common soil Mo extractant, presumably because it extracts amorphous Fe and Al oxides in the soil, with which much of the plant available Mo is associated (Gupta, 1997b). However, the use of ammonium oxalate has had varied success in predicting Mo responses (Sims and Eizazi, 1997).

Rhizosphere processes

While soil tests on bulk soils based on chemical extractants can be useful in predicting micronutrient supply to plants, major chemical and biological changes in the rhizosphere, induced by plant roots themselves, can have profound effects on chemical forms accessible to the roots and hence on uptake (Marschner, 1995). In addition, some of the changes are linked to the microbial population in the rhizosphere, which exceeds that in the bulk soil. The plant roots are the primary source of carbon (C) substrate for micro-organisms in the rhizosphere. Up to 14-40 % of C fixed by photosynthesis may end up released into the rhizosphere (Marschner, 1995). Micronutrient availability in the rhizosphere may be altered substantially compared to bulk soil through a number of mechanisms: pH change, release of soluble chelates, enzymes, organic acids and reductants or oxidants. Uptake of Fe, Mn, Zn and Cu is most profoundly affected. Some of these changes in the rhizosphere are triggered by deficiency in the plant, as a means to increase supply from the soil. Most of these changes in the rhizosphere are at least partly under genetic control in the plant and hence operate to varying degrees of efficiency in the rhizosphere of different cultivars. The form of N supplied has a major bearing on rhizosphere pH by influencing the cation-anion uptake ratio. When ammonium (NH_4^+) is the predominant form of N absorbed, cation uptake exceeds anion uptake and hence protons are excreted into the rhizosphere. By contrast, a predominance of nitrate (NO_3^-) uptake will tend to cause rhizosphere pH to increase. Such rhizosphere pH changes affect the availability and uptake of Zn, Fe and Mn in particular.

Considerable study on Fe has revealed a diverse range of rhizosphere processes affecting uptake. In non-graminaceous monocots and dicots, low Fe in the plant triggers a number of responses known as Strategy 1 responses. Strategy 1 responses comprise increases in proton and organic acid release into the rhizosphere, increased reduction of Fe(III) to Fe(II) for uptake, and root structural changes such as increased numbers of root hairs and transfer cells (Marschner, 1995). Rhizosphere pH may be as much as 2-3 units higher or lower than the bulk soil. Clearly, this has profound effects on Fe availability. These mechanisms increase Fe uptake but their effectiveness varies among species, cultivars and soils. For example, when soil pH is highly buffered, minimal pH decrease occurs in the rhizosphere, which only marginally increases Fe uptake. The relative importance of the different Strategy 1 responses for overall Fe uptake is not well understood (Rengel, 2001).

For graminaceous monocots, the release of phytosiderophores (PS) into the rhizosphere, coupled with a Fe(III)PS uptake system, known as Strategy 2, is the primary mechanism for enhancing Fe uptake on alkaline soils with low Fe availability. The susceptibility of graminaceous species to Fe deficiency can be predicted from the release of PS from roots under Fe deficiency. In general, the release of PS follows the series: barley > wheat > oat > maize > sorghum > rice (Marschner, 1995). However, cultivar differences in PS release are large enough to alter the above species ranking for a particular selection of cultivars. Strategy 2 is a more effective mechanism for Fe uptake on alkaline soil than Strategy 1, since the specific uptake system allows the complex to be absorbed without the need for reduction of Fe(III) in the apoplast before uptake. Phytosiderophores also enhance uptake of Zn, Mn and Cu. However, PS release is stimulated only in response to Zn deficiency (Zhang *et al.*, 1991).

Rhizosphere processes affecting Mn availability have been less well studied than for Fe (Rengel, 2001). Acidification of the rhizosphere is generally not sufficient in Mn deficient soil to account for increased uptake by efficient cultivars (Rengel, 2001). Preliminary studies suggest the Mn efficient barley and wheat cultivars generally have a greater population of Mn reducing bacteria. Rengel (2001) suggests that the composition of C compounds released into the rhizosphere may affect the dominance of Mn reducing *vs* Mn oxidising bacteria. It is postulated that the Mn efficient cultivars are able to maintain greater Mn availability in the rhizosphere by stimulating Mn reducing bacteria.

Mycorrhizal associations are important for uptake of soil immobile elements, phosphorus (P), Zn, Cu and Fe (Marschner, 1995). The hyphae of the fungal symbiont increase the effective surface area for nutrient absorption and explore a greater volume of soil than accessed by the non-mycorrhizal roots. The roots of most plants form mycorrhizal assocations, except where high soil P suppresses the symbiosis. Hence, in many well-fertilised agricultural soils, mycorrhiza levels are low, and this may limit uptake of Zn and Cu as well (Marschner, 1993). Inclusion of non-mycorrrhizal species such as sugar beet or linseed in crop rotations may induce deficiency of Zn in the subsequent crop by suppressing the mycorrhizal infection of roots (Leggett and Westermann, 1986 ; Thompson, 1990).

Topsoil *vs* sub-soil levels of micronutrients

Few studies have examined the sub-soil levels of micronutrients or the significance of sub-soil micronutrient uptake for crop nutrition. There are indications that roots in sub-soils may encounter micronutrient levels that are limiting to plant growth in the field (Graham and Ascher, 1993). The significance of low micronutrient levels in the sub-soil for crop demand depends in part on the adequacy of the topsoil levels and the ability of roots to extract micronutrients from the topsoil. However, Nable and Webb (1993) showed that Zn supply to the topsoil could not replace the need for Zn in sub-soil in order to achieve maximum growth of wheat. Dry topsoils may limit micronutrient uptake (e.g. Cu- Grundon, 1991), which forces plants to rely more on sub-soil uptake to supply plant requirements. The extent of remobilisation of the micronutrient in the plant plays a major role in sub-soil root growth in layers with low micronutrient levels (Loneragan *et al.*, 1987 ; Loneragan, 1988). Limited remobilisation of B and Mn occurs under most circumstances, while remobilisation of Fe, Cu and Zn depends on supply and plant N status (Robson and Pitman, 1983).

Wang *et al.* (1999) found that extractable B levels on key soils of south-east China declined with depth in the soil. Whereas extractable B in the 0-10 cm layer was 0.5 mg/kg, at 40-80 cm levels were 0.2 mg/kg. Follet and Lindsay (1988) examined profile distribution of Zn, Fe, Mn and Cu in Colarado soils. The study comprised 37 soil series, from a range of Soil Orders (Mollisol, Entisol, Alfisol and Aridisol). In general, DTPA extractable Zn, Fe, Mn and Cu decreased with depth in the profile even though total content of these micronutrients was relatively uniformly distributed in the profile. In 35 out of 37 profiles, the sub-soil DTPA Zn was at deficient levels. In fewer cases, sub-soil levels of Fe (6 out of 37), Mn (4 out of 37) and Cu (1 out of 37) were also low enough to be deficient for crop uptake. More comprehensive examination of sub-soil micronutrient levels is required to fully appreciate the significance of this limitation to micronutrient supply to crops. Low Zn levels in sub-soils could also restrict sub-soil water extraction (Nable and Webb, 1993), which in semi-arid cropping zones may be a more significant constraint to crop yield than the micronutrient deficiency, *per se*.

Additional reading

Adriano, D.C. (2001). *Trace Elements in Terrestrial Environments. Biogeochemistry, Bioavailability, and Risks of Metals*. 2nd ed. Springer-Verlag, New York.

Alloway. B.J. (ed.) (2008c). *Micronutrient Deficiencies in Global Crop Production*. Springer, Netherlands.

Fageria, N.K., Baligar, V.C. and Clark, R.B. (2002). Micronutrients in crop production. Advances in Agronomy 77: 185-268.

Lindsay, W.L. (1991). Inorganic equilibria affecting micronutrients in soils. pp. 89-112. In J.J. Mortvedt, F.R. Cox, L.M. Shuman and R.M. Welch (eds). *Micronutrients in Agriculture*, 2nd ed. SSSA Book Series No. 4. Soil Science Society of America, Madison, Wisconsin.

Marschner, H. (1995). *Mineral Nutrition of Higher Plants*, 2nd ed. Academic Press, London.

Stevenson, F.J. and Cole, M.A. (1999). *Cycles of Soil Carbon, Nitrogen, Phosphorus, Sulfur and Micronutrients*. 2nd ed. John Wiley and Sons, New York.

3. Micronutrients in plants, animals and humans

The importance of micronutrients in the health of plants (Marschner, 1995), humans and animals has been well known for many decades (Underwood and Suttle, 1999; McGuire and Beerman, 2007). However, the extent of micronutrient deficiencies in humans has only recently become a priority. The only defining characteristic of a micronutrient is its low concentration in most living tissues. However, the nutritional importance of micronutrients is high and does not reflect their low abundance. The essentiality for most micronutrients in plants, animals and humans has long been recognised but recent years have seen increased interest in the function and requirements of micronutrients, particularly in the field of human nutrition. Micronutrient malnutrition has been identified as a major underlying cause of numerous human health problems, particularly in developing countries with estimates of up to 2 billion people being affected by Fe deficiency alone (Gibson, 2006). It is necessary to understand the diverse range of functions micronutrients play in plants, animals and humans in order to understand their importance.

A large part of the functional role of micronutrients that are metals (e.g. Cu, Fe, Mn, Zn) is their involvement in metalloenzymes. Within enzyme systems, these metals play either structural or catalytic roles or can be required for enzyme activation as discrete cofactors. Metals in metalloenzymes are highly specific associations where loss of the metal results in a loss of catalytic activity and, in general, these metals cannot be replaced by any other. However, individual metalloenzymes are not always the domain of a single metal. Superoxide dismutase (SOD) for example is involved in the detoxification of the superoxide free radicle (O_2^-) by conversion into hydrogen peroxide (H_2O_2). Three SOD analogues exist (Mn-, Fe- and Cu-SOD), each using a different metal with similar properties for its catalytic function. Although they perform a similar function, the enzymes are not interchangeable as they are each localised to discrete areas of the cell.

The metals Fe, Cu, Mn and Mo are capable of valency change under normal biological conditions. Many enzymes utilize this property for their catalytic activity (see box below). Whilst not catalysing reactions themselves, other compounds such as the cytochromes and the Fe-S clusters also utilise the redox properties of these metals. These proteins usually share their electrons with enzymes that require redox chemistry thus forming redox chains, such as the role of cytochromes in the reduction of nitrate (NO_3^-) to ammonia (NH_3).

Examples of metalloenzymes with more than one valency:

Cu	superoxide dismutase (SOD), cytochrome oxidase, polyphenol oxidase
Fe	peroxidase, SOD
Mn	SOD
Mo	nitrate reductase, aldehyde oxidase, xanthine oxidase

Zinc differs from the other micronutrient metals in that it does not undergo redox transformation in biological systems. The catalytic role of Zn in enzymes is instead performed due to its strong Lewis acid chemistry. This, along with its stable structural properties has resulted in over 300 Zn metalloenzymes, far more than any other micronutrient.

Micronutrients are also involved in numerous other functions in plants, animals and humans including storage, transport and regulatory roles. Zinc plays a structural role in the 'Zn finger' domains, which act as DNA transcription factors in all eukaryotic cells. It has been estimated that 'Zn finger' domains may constitute up to 1 % of all human gene products. Further roles for trace elements in the regulation of gene expression are likely to be identified in the future as technology advances.

Compared to the other micronutrients, relatively little is known about the roles of B in plants, animals and humans. Boron has been recognised as an essential element in plants for many years, but only recently is it gaining acceptance as an essential element for animals and humans. So far, B has no known role in enzyme chemistry.

Boron

Functions

Plants Boron is required in the stabilisation of cell walls by forming the borate-rhamnogalacturonan II (RG-II, a complex pectic polysaccharide structurally located in the primary cell wall) cross-link (Matoh, 1997; O'Neill *et al.*, 2004). This primary function is reflected in the cessation of growth of young leaves and roots in response to B deficiency in plants (Dell and Huang, 1997). Boron also forms cross-links with glycolproteins in cell membranes and may regulate physical properties such as membrane fluidity. This may have implications in plant tolerance of high irradiance (Huang *et al.*, 2002) and low temperature stresses (Huang *et al.*, 2005). Although proposed B functions in the metabolism of phenols and lignin (Cakmak and Römheld, 1997) may be secondary effects (Cara *et al.*, 2002), B deficiency can influence lumber quality. Boron is essential for normal development of reproductive tissues and deficiency results in low grain set or poor seed quality (Dell *et al.*, 2002). Also, B deficiency may trigger the early synthesis of ethylene, leading to the rapid deterioration of fruit quality.

Animals and humans A large volume of information has become available about B effects on the health and nutrition of animals and humans in recent years (Nielsen, 2002; Devirian and Volpe, 2003; Hunt, 2003), but the primary functions of B at the cellular level remain enigmatic. Primary functions of B in animals and humans could be related to its binding with cellular membranes and biomolecules involved in various enzyme activities (Verstraeten *et al.*, 2005). It has been suggested that B may have a role in immune function (Hunt, 2003). Increasing evidence suggests that B may be an essential micronutrient in the metabolism of steroid hormones and some mineral nutrients (calcium (Ca), magnesium (Mg)) and vitamins (Devirian and Volpe, 2003; Hunt, 2003). It is well documented that dietary B intake improves bone strength in animals such as rats, chicken and pigs (Armstrong and Spears, 2001; Devirian and

Volpe, 2003), and that B is required for egg/embryo development in frog and zebrafish (Nielsen, 2002).

Requirements

Plants Plant B requirements have been updated in crop and forest species by using B-buffered solution culture or flowing solution culture. Critical B concentrations for the diagnosis of B deficiency during vegetative growth have been determined for a range of species (Bell, 1997; Bell *et al.*, 2002) (See box below).

Critical B concentrations (mg/kg dry weight) in the youngest open leaves:

soybean	10-12
oilseed rape	10-14
black and green gram	15-18
cassava	35
sunflower	12-20
bluegum	10-14
wheat	1.2

Animals and humans Boron requirements for animal and human health are less well defined, compared to those for plants. There is no established minimal intake recommendation for humans, but an upper intake limit for a person 19 years or older is considered to be 20 mg/day (Nielsen, 2002). Low dietary B intake (< 0.3 μg/g) adversely affects bone development, brain function, immune function and insulin secretion in chicks and rats (Nielsen, 1997). In humans, a daily supplementation of up to 3 mg of B is considered to help reduce bone loss and arthritis (Schaafsma *et al.*, 2001). A survey in the United States found that average B intakes for school children (4-8 years old) and adolescents (14-18 years old) were 0.80 mg/day and 1.02 mg/day, respectively; and for female and male adults, were 1.00 and 1.28 mg/day (Rainey *et al.*, 2002). Major sources of B in the human diet are fruits and vegetables (Devirian and Volpe, 2003). Given that broadleaf crops generally have higher B requirements and uptake than cereals (Bell, 1997), it is not surprising to find that fruits, vegetables, tubers and legumes are much better dietary B sources than grains of wheat, corn and rice .

Deficiency symptoms

Plants Boron-deficiency symptoms in plants have been described in numerous studies (Bell, 1997; see Chapter 13). In plants subject to mild B deficiency, leaves appear dark green and leathery with downward cupping and small size. When B deficiency becomes severe, dieback of the shoot tip occurs. Plant symptoms can be greatly influenced by other stress factors, such as high light intensity and low temperature. In reproductive parts, B deficiency causes abortion of flower buds and/or flowers (e.g. sterile ears in wheat), abnormally shaped fruits (e.g. avocado and citrus) and malformed seeds (e.g. hollow heart in peanut).

Animals and humans Despite a range of physiological effects of B dietary intake in animals and human, no specific B-deficiency symptoms have been observed.

Copper

Functions

Plants Copper plays important structural and functional roles in oxidative enzymes (such as SOD, cytochrome oxidase, ascorbate oxidase, polyphenol oxidase and diamine oxidase) and electron-transfer proteins (such as plastocyanin in chloroplasts). Due to these functions of Cu in plants, physiological consequences of Cu deficiency may include inhibition of photosynthesis and low availability of soluble carbohydrates in leaves (Marschner, 1995). Another distinct function of Cu is the role of several Cu-metalloenzymes in the lignification of cell walls. Lignified walls are required for support, water transport and release of pollen.

Animals and humans Copper is essential for the immune system, the nervous system, skeletal health, for Fe metabolism and for formation of red blood cells (Johnson, 1998). As in plants, Cu is involved in redox reactions and the scavenging of free radicals. It is a component of more than 12 metalloenzymes and a few genes are known to be regulated by Cu-dependent transcription factors (Uauy *et al.*, 1998). The mitochondrial enzyme, cytochrome c oxidase, plays a critical role in cellular energy production by reducing oxygen to water, which generates an electrical gradient allowing the formation of the energy-storing molecule, adenosine triphosphate (ATP).

Ceruloplasmin and Cu-SOD function as antioxidants that scavenge for free radicals. Lysyl oxidase is essential for the cross-linking of collagen and elastin and helps maintain the integrity of connective tissue in the heart and blood vessels, and skeletal system. Ferroxidase II catalyses the oxidation of Fe(II) to Fe(III), which facilitates transport to sites of red blood cell formation. Several cuproenzymes are important for normal function of the central nervous system including dopamine beta-hydroxylase and monamine oxidase. Tyrosinase is required for the formation of the pigment melanin.

Requirements

Plants In general, critical Cu levels in vegetative growth lie in the range of 1-5 mg/kg dry matter (Marschner, 1995), but different species may have different requirements (Reuter and Robinson, 1997; Dell *et al.*, 2001). Plant reproduction may have higher Cu requirements than vegetative growth.

Animals and humans The diet of cattle (pasture, range, hay, etc.) should contain about 4-10 mg Cu/kg to supply the needs of cattle. Less than this amount may result in Cu deficiency. The absorption of Cu is sensitive to the presence of dietary antagonists, particularly Fe, Mo and sulphur (S). Excessive Mo can induce secondary Cu deficiency by combining with Cu and S in the rumen to form the insoluble product, copper thiomolybdate. Concentrations as low as 0.5 mg Mo/kg dry matter (DM) in pasture may have a significant effect on Cu absorption, much lower than earlier estimates (Lee *et al.*, 1999).

The Recommended Dietary Allowance (RDA) established by the US Food and Nutrition Board (USFNB, 2001) for children aged 4-8 is 440 μg Cu/day, and 900 μg Cu/day for males and females 19 years and older. Dietary factors known to inhibit Cu absorption in humans include ascorbic acid, phytates, sucrose, fructose, Zn and Fe, but the effects are only seen at very high intake levels and are thought to be of little practical significance in normal diets. The possibility exists however, that some factors may affect Cu absorption from atypical diets e.g. in countries where the diets have a high phytate component or when taking Zn supplementation (USFNB, 2001).

Deficiency symptoms

Plants The most typical anatomical change induced by Cu deficiency is the distortion of young leaves, stem bending and twisting and lodging (in cereals) (Marschner, 1995). Leaf chlorosis can occur at the onset of Cu deficiency followed by twisting and cupping in young leaves and leaf death (Grundon *et al.*, 1997). In fruit trees, an early sign of Cu deficiency is the pendulous habit of lateral branches and during reproduction, increased production of sterile pollen (Grundon *et al.*, 1997). In timber trees, snake-shaped trunks and sparse canopies are common early signs of Cu deficiency (Dell *et al.*, 2001).

Animals and humans Copper deficiency is well known in farm animals. Symptoms include loss of coordination of the hind limbs in lambs due to impaired development of the central nervous system, sudden death in cattle due to heart failure, and de-pigmentation of the hair around eyes in cattle and of black wool in sheep (McDowell, 2003). Poorly crimped wool in sheep, poor weight gains, diarrhoea and fragile bones occur but are not specific to Cu deficiency. Copper deficiency lowers the immune response and makes animals more susceptible to disease. Liver Cu concentration is one of the best indicators of Cu status and blood serum levels are generally only useful where deficiency is severe.

Copper deficiency in humans is rare (Turnlund, 1999) and most cases have been described in malnourished children. The most frequent clinical manifestations of Cu deficiency are anemia, neutropenia (low white blood cell count) and bone abnormalities. Less common symptoms can include abnormal glucose tolerance, loss of pigmentation and neurological problems (Uauy *et al.*, 1998). Cow's milk is relatively low in Cu, and cases of Cu deficiency have been reported in high-risk infants and children fed only cow's milk formula.

Iron

Functions

Plants Iron is essential for many biochemical and physiological processes in plants including the utilization of N and S, the production of the plant hormone ethylene, the biosynthesis of chlorophyll and the composition of some cell walls. Iron(II) is an electron donor and hence is a key constituent of electron-transport chains. Iron is stored as Fe(III), mostly as phytoferritin, and is reduced to Fe(II) for physiological function in the cell. Iron is generally incorporated into heme and non-heme proteins. The most well-known heme proteins are the cytochromes, which contain a heme Fe-porphyrin complex (Marschner, 1995).

In legume nodules, a related class of compounds, the leghemoglobins, regulate the supply of oxygen to the bacteroids responsible for fixation of N. The bacterial nitrogenase enzyme, which reduces N_2 to NH_3, consists of two metalloproteins, the Fe protein (dinitrogenase reductase) and the FeMo protein (dinitrogenase) (Bosch and Imperial, 2000).

Other heme proteins are involved in the formation of lignin and suberin (peroxidases), and the breakdown of H_2O_2 to water and oxygen (catalases). The most common non-heme proteins contain Fe-S clusters, which serve as cofactors for redox, catalytic and regulatory functions. Examples of Fe-S proteins are ferredoxin and Fe-SOD. Ferredoxin is an electron carrier assisting enzymes involved in the reduction of nitrite (NO_2^-) and sulphite (SO_3^{2-}), and biological N_2 fixation, and is an essential component of the electron transport pathway in photosynthesis.

Animals and humans Iron is essential for humans and animals. It plays a central role in metabolic processes involving oxygen transport and storage as well as oxidative metabolism and cellular growth. About 85 % of body Fe is a constituent of two heme proteins: hemoglobin, essential for transferring oxygen in the blood from the lungs to tissues; and myoglobin, the oxygen store in muscles. A number of other heme proteins are enzymes and include the cytochromes involved in energy production in the mitochondria, and peroxidases that degrade reactive by-products of oxygen metabolism.

Non-heme proteins can store and transport Fe (ferritin, transferritin) or function as enzymes (metalloflavoproteins, Fe-S proteins, ribonucleotide reductase). Examples of Fe-S proteins are NADH dehydrogenase and succinate dehydrogenase that play roles in energy metabolism (Yip and Dallman, 1996). In adult men, about one third of the total body Fe is stored Fe, whereas, in women, storage accounts for about one eighth of total body Fe (Yip and Dallman, 1996). Dietary Fe overload can cause acute Fe poisoning as the body has no adjustable Fe excretory mechanism (Lynch, 2003a).

Requirements

Plants Critical deficiency concentrations for Fe in leaves typically range from 50–150 mg Fe/kg although levels may be marginally greater in C_4 plants (Marschner, 1995). Iron deficiency is common on calcareous and high pH soils due to impaired Fe acquisition commonly known as 'lime-induced chlorosis'. Diagnosis of Fe deficiency by plant analysis is limited, since there is often no relationship between total leaf Fe content and deficiency symptoms. Moreover, Fe concentrations in chlorotic leaves are frequently greater than those in healthy green leaves. This phenomenon, known as the 'chlorosis paradox', is caused by inactivation of Fe in the leaf.

Animals and humans Hemoglobin accounts for approximately 60 % of body Fe. For this reason, the Fe requirements of livestock vary with age and level of activity. Iron requirements decline with age because as animals grow, increase in red-cell mass constitutes a progressively smaller component of weight gain. Supplementation of pre-starter and starter diets is widely used in the livestock industry as milk alone is often not sufficient to supply Fe. Non-working animals may not be adversely affected by mild anaemia, however, it is recommended that Fe levels be maintained within adequate limits as deficiency may lead to increased absorption of potentially harmful elements such as Cd and Pb (Underwood and Suttle, 1999).

For humans, RDAs have been estimated based on the need to maintain a normal, functional Fe concentration, but only a minimal store. The USFNB (2001) gives a RDA of 10 mg Fe/day for children (4-8 years), 8 mg/day for adult (31-50 years) males and 18 mg/day for females. RDAs are based on an estimated Fe bioavailability of 18 % in the average North American diet.

Iron bioavailability is largely determined by the two main dietary Fe forms: heme and non-heme. Heme Fe is readily bioavailable and dietary factors have little effect on absorption. Non-heme Fe on the other hand is absorbed through a separate pathway, which requires the reduction of the predominantly Fe(III) to the Fe(II) form. Reduction and subsequent absorption can be greatly increased by the presence of ascorbic acid (Vitamin C) in the diet. Conversely, phytates and phenolic compounds can inhibit absorption through the formation of stable ferric complexes. The main sources of heme Fe are haemoglobin and myoglobin in red and white meats and fish. Non-heme Fe is present in plant and dairy products.

Deficiency symptoms

Plants Iron deficient leaves typically develop interveinal chlorosis and, when deficiency is acute, the whole leaf takes on a bleached appearance and necrotic lesions may develop (see Chapter 13). Because of restricted phloem mobility of Fe, symptoms usually progress from young to mature leaves. Examples of symptoms are illustrated in Bergmann (1992) and Dell *et al.* (2001). Iron deficiency is particularly severe on calcareous soils.

Animals and humans Iron deficiency seldom occurs in farm animals as there is usually adequate Fe intake in the diet (Underwood and Suttle, 1999). However, Fe deficiency can occur in animals reared in confinement primarily on milk or due to severe loss of blood caused by parasitic infestations, injury or disease. Symptoms of Fe deficiency include anemia (inadequate number of red blood cells), poor growth, listlessness, laboured breathing after mild exercise, rough hair coat and paleness of mucous membranes (McDowell, 2003).

A lack of Fe is the most common nutritional disorder in humans, with estimates ranging from 500 million (Lynch, 2003a) to 2 billion (Stolzfus and Dreyfuss, 1998) people affected worldwide. Iron deficiency is most prevalent in the developing world. According to EVM (2002), people most vulnerable to Fe deficiency are: infants greater than six months, toddlers, adolescents and pregnant women due to high requirements; the elderly and people consuming foods high in inhibitors of Fe absorption; and menstruating women or individuals with pathological blood loss due to high Fe losses. Iron deficiency results in anemia (Lynch, 2003b).

The main clinical symptoms include pallor, fatigue, weakness, dizziness, reduced intellectual performance and reduced maximal work capacity (Yip and Dallman, 1996; Lynch, 2003a). Iron-deficiency anemia is associated with impaired mental development and physical coordination in children under the age of 2 years (Beard and Connor, 2003; Lynch, 2003a). Behavioural changes include reduced attention span and reduced emotional responsiveness (Hulthen, 2003).

Manganese

Functions

Plants Manganese is essential for photosynthesis in all plants as the Mn_4Ca cluster (Rutherford and Boussac, 2004) is part of the catalytic centre for the light-driven water oxidation in photosystem II, commonly known as the Hill reaction. The main enzyme known to contain Mn is SOD. Manganese is an activator of a large number of enzymes that catalyse oxidation-reduction, decarboxylation and hydrolytic reactions. Through these enzymes, Mn plays a role in the production of lignin, flavonoids, fatty acids, indole acetic acid and other pathways. It can also affect N metabolism. In C_4 plants (e.g. maize) and plants that fix their carbon at night, Mn is essential for CO_2 assimilation because it activates the enzyme phosphoenylpyruvate carboxylase (Mengel and Kirkby, 2001).

Animals and humans Like in plants, Mn functions as a constituent of metalloenzymes and as an enzyme activator in animals and humans (Nielsen, 1999; Keen and Zidenberg-Cherr, 1999). The metalloenzymes include: Mn-SOD; pyruvate carboxylase, which is required for gluconeogenesis (carbohydrate synthesis from pyruvate); and arginase, which is required by the liver for urea formation. There are a large number of enzymes, which are activated by Mn, either by the Mn binding to the protein or to the substrate: glycosyltransferases are required for the synthesis of proteoglycans in bone and cartilage; phosphoenolpyruvate carboxykinase is required for gluconeogenesis; glutamine synthetase is required for the assimilation of NH_3 and in N metabolism; and prolidase produces proline for collagen in skin.

Requirements

Plants The critical deficiency concentrations for Mn vary little among plant species. Typical values range between 10 to 20 mg/kg in fully expanded leaves (Marschner, 1995), with the exception of narrow-leaf lupin, which may be up to double this (Hannam and Ohki, 1988). Deficiencies commonly occur on soils derived from parent materials low in Mn, highly leached tropical soils and alkaline soils, particularly when combined with high levels of organic matter.

Animals and humans Manganese requirements of sheep and cattle are quite low, and pastures rarely fail to meet requirements. Manganese deficiency can be a problem in domestic animals such as pigs, poultry and non-grazing ruminants due to protein supplements being low in Mn. Inorganic supplements such as $MnSO_4$, MnO and $MnCO_3$ are commonly used for the treatment and prevention of deficiency.

The human requirement for Mn is very low, and even during prolonged total parenteral nutrition (TPN) no clear evidence of deficiency has emerged. However, because of the potential importance of Mn, additives containing this element have been included in TPN regimens.

Widespread Mn deficiency has not been shown to occur in humans eating natural diets. USFNB has set an adequate intake level based on average dietary Mn intakes, which in the USA range from 2.1-2.3 mg/day for men and 1.6-1.8 mg/day for women. Rich sources of Mn include whole grains, nuts, leafy vegetables and teas. Absorption of Mn is reduced by the presence of phytate, oxalate and tannins.

Deficiency symptoms

Plants Though symptoms of Mn deficiency vary among crop species, the most common are interveinal chlorosis and discoloured spots (Bergmann, 1992; see Chapter 13). Symptoms progress from young to mature foliage. Reduced lignification of the xylem can lead to wilting of leaves and impaired wood development. Other symptoms observed include split seed in lupins, impaired pollen development, delayed maturity and reduced yields. Deficient plants may show increased susceptibility to disease (Graham and Webb, 1991).

Animals and humans Manganese deficiency has not been reported for humans. In experimental animals, dietary Mn deficiency can result in numerous biochemical and structural abnormalities. Deficient animals can be characterized by impaired insulin production, alterations in lipoprotein metabolism, an impaired oxidant defence system, and perturbations in growth factor metabolism. If the deficiency occurs during early development, there can be pronounced skeletal abnormalities and abnormal inner ear development (Keen *et al.*, 1999). The most common symptoms observed in livestock are impaired reproductive performance, skeletal deformities and shortened tendons in the new born (McDowell, 2003).

Molybdenum

Functions

Plants Molybdenum, when inserted as part of a prosthetic group known as the Mo-cofactor, is required for the function of a few enzymes involved in redox processes (Mendel and Haensch, 2002; Sauer and Frebort, 2003). Nitrate reductase is essential for the reduction of NO_3 before it can be assimilated in plants. Aldehyde oxidase is involved in the synthesis of the hormones indole-3-acetic acid and abscisic acid. Xanthine dehydrogenase is required for purine catabolism and the synthesis of ureides in soybean and cowpea (Marschner, 1995). Molybdenum is also required by bacteria in root nodules as a component of the Mo-Fe sub-unit of nitrogenase, which is essential for biological N_2 fixation.

Animals and humans Molybdenum is essential for the function of a number of enzymes involved in important transformations of C, N and S (Hille, 1999). In humans, Mo is a cofactor for three enzymes: sulphite oxidase, xanthine oxidase and aldehyde oxidase. Only sulphite oxidase is known to be crucial for human health (Nielsen, 1999). Sulphite oxidase converts sulphite to sulphate, a reaction that is necessary for the metabolism of S-containing amino acids.

Requirements

Plants On soils low in Mo or where the molybdate anion is strongly adsorbed, crops dependent on NO_3-N and legumes are most likely to benefit from application of Mo fertiliser (Kaiser *et al.*, 2005). The critical deficiency concentrations of Mo in young mature leaves of soybean and peanut are 0.02 and 0.015-0.05 mg/kg, respectively. Higher concentrations are required in the nodules (>7 mg/kg in peanut).

Animals and humans The minimum requirement is unknown for most animal species. In humans, the essentiality of Mo is based on a genetic defect that prevents sulphite oxidase synthesis (USFNB, 2001). The RDA for adult men and women is 45 μg/day (USFNB, 2001). Care must be exercised when applying Mo fertiliser to pasture and other animal foodstuffs as excess dietary intake of Mo can lead to Cu deficiency (molybdenosis) in ruminants.

Deficiency symptoms

Plants Leaves of Mo-deficient plants usually show symptoms of N deficiency (chlorosis) (see Chapter 13). Symptoms frequently appear on mature leaves. However, in some species, abnormal growth such as stunting, reduced leaf blade (whiptail in cauliflower) and curling of leaf margins can occur. Marginal chlorosis/necrosis occurs where nitrate concentrations become excessive in leaves. Deficiency is most common in legumes on acid soils. Molybdenum deficiency has been reported to disturb reproductive development and reduce grain yield in cereal crops (Chatterjee and Nautiyal, 2001) and cause berry disorders in grapes (Williams *et al.*, 2004). It has been suggested that Mo can indirectly alter the resistance of some plants to disease (Graham and Stangoulis, 2005).

Animals and humans Molybdenum deficiency has not been identified in free-living animals. A Mo-deficient diet was associated with reduced fertility and increased mortality in goats (Auza *et al.*, 2002). Rare genetic deficiency of the Mo cofactor usually results in premature death in early childhood (USFNB, 2001).

Zinc

Functions

Plants Zinc has a diverse range of roles in plants being required for protein synthesis, gene regulation, structure and integrity of biomembranes, the protection of cells from oxidative damage and other roles. Under Zn deficiency, protein synthesis is depressed because of reduced levels of RNA due to the essential role of Zn in RNA polymerase. Furthermore, the role of 'Zn fingers' in DNA transcription and gene regulation also contribute to Zn's function in protein synthesis. The importance of Zn in protein synthesis results in a high Zn requirement in meristematic tissues.

Zinc deficiency reduces net photosynthesis, although the exact cause is unknown. In C_4 plants, such as maize, the Zn-dependent enzyme carbonic anhydrase is required in photosynthesis to provide HCO_3^- as a substrate for phosphoenol pyruvate carboxylase. Carbonic anhydrase does not have a specific role in photosynthesis in C_3 species such as rice.

Zinc has an essential role in both plants and animals in the structure and function of bio-membranes. In plants, this may manifest as 'leakiness' of roots. Under Zn deficiency, roots have been observed to exude greater amounts of amino acids, phenolics and other compounds. Zinc plays a key role in controlling the generation and detoxification of reactive oxygen species (ROS) (Cakmak, 2000). Oxidative damage is responsible for some of the characteristic symptoms of Zn deficiency caused by the oxidative degradation of the growth hormone, auxin.

Animals and humans Many of the generic functions of Zn described earlier for plants, such as Zn-metalloenzymes, and 'Zn fingers' also apply to animals and humans. Thus, Zn is essential for DNA and protein synthesis, cell division and growth. Zinc is required for male and female reproduction and neurological function. Zinc is also essential for immune function and deficiency impairs resistance to infection (Walker and Black, 2004). Zinc may be important in host defence against cancer (Ho, 2004).

Requirements

Plants Critical deficiency concentrations are typically between 15-20 mg/kg in young leaves (Marschner, 1995.) This however may vary to as low as 7 or as high as 30 mg/kg, depending on the species and stage of development (Reuter and Robinson, 1997). Deficiencies may be particularly prevalent in species such as beans, maize and rice, which are sensitive to low Zn (Alloway, 2008a). Critical Zn concentrations (mg/kg dry weight) in the youngest expanded leaves for the diagnosis of Zn deficiency range from 11-14 in wheat, 11-15 in corn and 10-22 in soybean.

Animals and humans Zinc requirements of animals vary widely among species, with age and composition of the diet. Dietary factors, particularly phytate and protein, affect bio-availability of Zn. Absorption of zinc may be adversely affected if the Ca and P levels in the ration are very high.

As much as one third of the world's population may be at risk from inadequate Zn uptake according to the International Zinc Nutrition Consultative Group (IZiNCG). USFNB (2001) sets its RDA at 5 mg/day for children (4-8 years), 11 mg/day for adult (31-50 years) men and 8 mg/day for women. Whole grains, lean meats and legumes are good sources of Zn with concentrations ranging between 25 and 50 mg/kg although other dietary factors, especially phytate and dietary protein, may influence actual Zn absorption.

Phytates are present in cereals, legumes and small amounts are found in some vegetables. The molar ratio of phytates and Zn in the diet is a useful indicator of the inhibitory effect of phytates on Zn absorption (Sandstrom and Lonnerdal, 1989). Adverse effects become apparent at molar ratios above the range of 6-10. At a ratio of 15, Zn absorption is typically less than 15 %. Dietary protein on the other hand has the opposite effect and can improve Zn absorption from a high phytate diet (Sandstrom and Lonnerdal, 1989).

Other minerals such as Cu, Fe and Ca may competitively inhibit Zn absorption, but these are only thought to be a risk when taken at high dosages, in the form of supplements or aqueous solutions, for example. In a joint publication by the Food and Agriculture Organization of the United Nations (FAO) and the World Health Organization (WHO) (FAO/WHO, 2005), the recommended nutrient intake (RNI) is further divided into high, moderate and low bioavailability corresponding to an adsorption efficiency of 50 %, 30 % and 15 %, respectively, depending on the Zn source. For children aged 4-9, RNI ranges from 2.9 to 11.2 mg Zn/day for high and low bioavailability, respectively. Strategies for identifying countries at risk and targeted Zn interventions are discussed by Gibson (2006).

Deficiency symptoms

Plants Zinc deficiency symptoms are first expressed in the young, expanding leaves reflecting the low phloem mobility of Zn in the plant. 'Little leaf' is a characteristic symptom of acute Zn deficiency in many species. In broad-leaf crops, this is accompanied by reduced internodal length known as rosetting. Other symptoms include interveinal chlorosis and upward cupping of leaves. In grasses and cereals, a chlorotic stripe may appear adjacent to the midrib. Brown necrotic spots are often associated with Zn deficiency but are caused by the excessive uptake of P. Zinc deficiency can severely reduce fruit and grain yield. Symptoms have been illustrated in many works (e.g. Bergmann, 1992; Dobermann and Fairhurst, 2000; Alloway, 2008a; 2008c; see Chapter 13).

Animals and humans Zinc deficiency in livestock is manifested by reduced growth rate, reduced fertility, thickening and scaling of skin cells, dermatitis, hair loss and increased susceptibility to foot infections. Zinc deficiency also interferes with Vitamin A in the liver. Deficiencies in the field are known for cattle, sheep, goats, pigs and poultry (McDowell, 2003).

Due to the central role of Zn in cell division, protein synthesis and growth, Zn is particularly important for young children, adolescents and pregnant women. Symptoms of severe Zn deficiency include skin lesions, dwarfism, delayed onset of puberty and diarrhoea (Hambidge, 2000; FAO/WHO, 2005).

Other micronutrients

Cobalt is essential for plants dependent on symbiotic N_2 fixation. The critical deficiency concentration for narrow-leaf lupin seed is 0.13 mg Co/kg (Robson and Snowball, 1987). Cobalt is also required by the rumen microflora of ruminants for the synthesis of vitamin B12. Deficiency causes a serious wasting syndrome in sheep and cattle. Vitamin B12 is essential in the human diet as well. Baik and Russell (1999) estimated that some 10-50 % of humans over the age of 60 are affected by vitamin B12 deficiency. As mentioned in Chapter 1, Ni is an essential element for plants (Brown *et al.*, 1987). Symptoms of Ni deficiency in pecan are shown in Chapter 13.

Additional reading

Alloway, B.J. (ed.). (2008c). *Micronutrient Deficiencies in Global Crop Production*. Springer, Dordrecht.

FAO/WHO (2005). *Vitamin and Mineral Requirements in Human Nutrition*, 2nd ed. Food and Agricultural Organization of the United Nations (FAO) and World Health Organization (WHO), Rome and Geneva.

Marschner, H. (1995). *Mineral Nutrition of Higher Plants*, 2nd ed. Academic Press, London.

McDowell, L.R. (2003). *Minerals in Animal and Human Nutrition*, 2nd ed. Elsevier Science BV, Amsterdam.

Mengel, K. and Kirkby, E.A. (2001). *Principles of Plant Nutrition*, 2nd ed. Kluwer Academic Publishers, Dordrecht.

Sharma, C.P. (2006). *Plant Micronutrients*. Science Publishers, Enfield.

Underwood, E.J. and Suttle, N.F. (1999). *The Mineral Nutrition of Livestock*. CABI Publishing, New York.

4. Benefits of using micronutrient fertilisers

The benefit that most producers seek from using micronutrient fertilisers is an increase in income due to increased yield or quality of harvested products. In the most severely deficient soils, the application of micronutrient fertiliser makes an absolute difference between being able to use land productively for agriculture, horticulture or forestry, or not. Over eight million hectares (ha) of such land in southern Australia was brought into grain and pasture production in the 1950s when it was recognised that micronutrient deficiencies (Zn, Cu and Mo) were a major constraint to profitable yields, and that simple, cost-effective treatments were available (Donald and Prescott, 1975). The increase in harvested area in developing countries is projected to continue into the future requiring a total of 120 million ha of new cropping land by 2030 (Alexandratos, 2005). The vast majority of this land is in sub-Saharan Africa and Latin America (Alexandratos, 2005). Land managers, extension officers and researchers need to remain vigilant for the possibility of acute micronutrient deficiencies when new land is developed for agriculture, or where land undergoes major land use changes otherwise yield potentials will not be achieved and sustained on such sites in the future.

We are familiar with severe micronutrient deficiencies that arise following clearing of primary and secondary forests in many upland areas in Asia and, no doubt, similar issues will occur elsewhere due to infertile soils and loss of soil fertility. Examples include B deficiency after clearing in parts of Sumatra, Mindanao, Hainan and Yunnan, Fe deficiency in west Sumatra and central Thailand, Zn deficiency in south China, and Cu deficiency in Indonesia. When shrubland was cleared for bluegum plantations near Chuxiong (west of Kunming), in the mid 1990s, B deficiency was so severe that trees grew horizontally (see Chapter 13).

Field crops

On deficient soils, the effect of micronutrient fertiliser application is to increase yield. It is difficult to establish what production yield increase to attribute to micronutrient fertilisers when applied in production fields. However, from research, there are abundant examples of strong increases in yield. Rashid and Ryan (2004) summarise reported cases of crop responses to Zn, Fe and B in Mediterranean-type soils. Shorrocks (1997) notes that there were 500 reported cases of B fertiliser responses globally, spread across 80 countries and found in 132 crop species. The land area treated with B fertiliser was 3-4 million ha in Europe, 3.7-5 million ha in Australasia, 0.6-1 million ha in Africa and 6-8 million ha in the Americas (Shorrocks, 1997).

One of the most spectacular recent cases of micronutrient fertiliser having a major impact on crop production has been the adoption of Zn fertilisers in Turkey starting from nil in 1994 to 350,000 tonnes in 2006 (Cakmak, 2008a). Following the first field trial evidence in 1992 (Cakmak, 2008b) that Zn fertiliser resulted in substantial wheat yield increases in the Central Anatolia region, there has been rapid adoption of Zn fertilisers in Turkey. Zinc is now applied as an additive in NPK or NP fertilisers during the granulation process at the concentration of 1 % Zn w/w. The economic benefit of the use of Zn fertiliser is estimated to be US$ 100 million (Cakmak, 2004). In addition, the substantial increases in grain Zn content resulting from the widespread use of Zn fertilisers will have improved human health by boosting Zn intake and bioavailability in the diet.

Pakistan is an example of a country that has more recently established that low micronutrient levels in soils are widespread and that crop responses are possible from greater use of micronutrients in agriculture (Rashid, 2006). Of the 22 million ha of cultivated land, most is calcareous alluvium and loess material. Hence deficiencies of Zn, B and Fe are most common. Copper and Mn deficiencies are more localised and, because of high pH, no cases of Mo deficiency have been reported for Pakistan. Average yield increases reported for a range of crops in field trials are greater than those reported in China (Tables 4.1 and 4.2). Moreover, the benefit:cost ratios from using Zn, B and Fe fertilisers were in the range 8 to 264, suggesting large pay-offs from the adoption of this technology.

Table 4.1. Crop responses to Zn and B fertilisers in field trials in Pakistan. (Anonymous, 1998).

Crop	Province	Rate applied (kg/ha)	% increase	Benefit:cost ratio
			Zn	
Rice	Punjab, Sindh, NWFP	5-7.5	10-12	6-10
Wheat	Punjab, NWFP	2.5-10	13-14	5-7
Corn	Punjab, NWFP	5	18	9
Cotton	Punjab, Sindh	5	8	12
Sugarcane	NWFP	10	8	8
Potato	Punjab, NWFP	5	22	50
			B	
Rice	Punjab, Sindh, NWFP	1-2	20	22-45
Wheat	Punjab, NWFP	1-2	14	4
Corn	Punjab, NWFP	1-1.5	20	7
Cotton	Punjab, Sindh, NWFP	1-2	14	15
	Punjab	Foliar sprays	12	30
Sugarcane	NWFP	Foliar sprays	40	30
Potato	NWFP	1.5-2	21	19
	Punjab	Foliar sprays	26	264
Peanut	Punjab	1	10	11

Rates of nutrient application in the foliar sprays were not reported.

Rashid (2006) estimated that the potential net benefits from B fertiliser use alone on 50 % of the crop area for cotton, rice, maize and wheat would be worth US$ 125 million per annum. However, the 2006 trade in micronutrient fertilisers in Pakistan was very small and there were concerns about the poor quality of some products in the market. There clearly remains a significant gap between research evidence of the need for micronutrient fertilisers, the farmers' knowledge of the opportunity to increase production and the market, which has so far failed to develop and supply appropriate, cost-effective products. Recently several private companies have shown interest in producing and distributing micronutrient fertilisers in Pakistan.

In the 1980s, a national soil analysis programme in China determined the risk of micronutrient deficiency (Liu, 1992). It found a very high proportion of soils in northern China were low in Zn, while in southern China low soil B was more prevalent. The prevalence of low Fe and Mn in soils was lower overall than for Zn and B, but was greatest in northern China. A follow-up soil analysis programme carried out in 2002 (Jin *et al.*, 2006), involving 25,285 soil samples from 31 provinces, was carried out to determine how fertiliser and land use practices in the intervening 20 years had affected the levels of micronutrients in soils. The 2002 soil analysis survey established that micronutrient levels remain low in a large proportion of Chinese soils. In northern China, the percentage of soils with low Zn, B, Fe, Mn and Cu was 71, 17, 36, 25, and 13 %, respectively. For southern China, the percentage of soils with low Zn, B, Fe, Mn and Cu was 48, 34, 5, 16, and 10 %, respectively. A limited programme of field experiments verified that yield responses to micronutrients are still common (Table 4.2). Hence, even

Table 4.2. Average yield responses to micronutrient fertilisers in field experiments conducted in China (Jin *et al.*, 2006).

Micronutrient	Crop	Rate of application	Yield response (% increase)
Zn	Corn	15 kg $ZnSO_4$/ha	2-15
	Cotton lint		10
	Cotton seed		9
B	Corn	15 kg boric acid/ha	17
	Cotton lint		11
	Cotton seed		10
	Rapeseed	7.5 boric acid/ha	6
Fe	Peanut	FeEDDHA spray	10-11
Mn	Corn	30 kg $MnSO_4$/ha	2-8
	Cotton lint		13
	Cotton seed		11
Cu	Corn	5.2 kg $CuSO_4$/ha	29

Rate of nutrient application in the foliar spray was not reported.

though low micronutrient levels in Chinese soils, that are sufficiently low to affect crop production, has been known for over 20 years, there remains a significant opportunity to capture greater benefits for agricultural production in China by increased use of micronutrient fertilisers on soils.

In India, boronated NPK (10:26:26, $N:P_2O_5:K_2O$) fertilisers have been introduced to the market, as an attempt to improve the distribution of B fertiliser to farmers in a form that minimises dependence on large-scale extension programmes (Phillips, 2006). The rate of B addition in the boronated NPK (0.3 %) was sufficient to correct deficiency but avoids the risk of toxicity, which can occur if farmers apply B fertilisers alone without proper care to spread it evenly or without awareness of the optimal rate. Yield increases on farmers' fields with the boronated NPK, across a wide range of crops, including field crops, rice, vegetables and fruit trees, were 5-29 %. Ninety-seven % of 366 farmers involved in the field evaluations of the boronated NPK observed growth improvements in their crops with boronated NPK, and almost all of these farmers indicated that they would be prepared to purchase the boronated product next year even though it costs more than the equivalent non-enriched product. The benefit:cost ratios were in the range 12-68 for the boronated NPK (Phillips, 2006).

In India, a major soil analysis programme over the period 1967-1983 resulted in the testing of 89,000 samples (Singh, 2004). These revealed > 50 % of samples had potentially deficient Zn levels. A follow-up survey from 1984-1997 comprising 67,000 soil samples indicated a substantial decrease in the percentage of low-Zn soils. The decline in incidence of low-Zn soil samples was attributed to the adoption of Zn fertiliser. However, 18-48 % of soils samples, depending on the state, still had low soil Zn, which would potentially produce deficiency in crops. In addition, 64 % of 5,823 on-farm trials conducted across India showed yield responses to Zn fertiliser in a diverse range of species (Singh, 2004). This indicates that further adoption of Zn fertiliser use on farms in India would capture additional benefits. Interestingly, over the 15-20 year period, when Zn fertiliser came to be used more commonly, deficiencies of Mn and Fe emerged in the intensive rice-wheat cropping system.

In most cropping systems, the main benefit from use of appropriate rates and types of micronutrient fertilisers will be to increase the use efficiency of N, P and K fertilisers. In crop production, NPK fertilisers are one of the largest variable costs and, therefore, maximising the benefit from using this input has significant value to producers. When recommended rates of NPK are added to crops that suffer marginal micronutrient deficiency, fertiliser is wasted because crops cannot achieve their yield potential. In situations where off-site effects of excess N and P are possible, the unused fertilisers may contribute to environmental degradation in surface and groundwater resources.

Vegetables and horticulture

Micronutrients are used in production of vegetables and fruit trees not only to avoid yield loss but also to improve product quality. The impaired quality of the harvested product due to micronutrient deficiency often causes greater economic losses than from decreased yield especially for fruits and vegetables. In peanut, for example, only

2 % or more hollow heart incidence in kernels downgraded the price in US markets (Morrill *et al.*, 1977). Storage of fruits may also be impaired by low B levels. In avocado, for example, Smith *et al.* (1997) showed that B application increased fruit size and the time to ripening by 4-5 days, and both of these attributes improved marketability of the fruit.

Boron deficiency in particular causes low quality of harvested products in a range of species:

- internal fruit necrosis in mango (Ram *et al.*, 1989);
- brownish discolouration of cauliflower curds (Kotur, 1991);
- premature staining of the testa in avocado (Harkness, 1959);
- internal and external corking of fruit tissue in apples (Shorrocks and Nicholson, 1980);
- lesions in storage organs of sugar beet and rutabaga (Gupta and Cutcliffe, 1972; Vlamis and Ulrich, 1971).

Forestry

In forestry, micronutrient fertilisers are beneficial in increasing wood volumes. In addition, micronutrient fertiliser application may improve tree form and wood quality (Stone, 1990 ; Dell *et al.*, 2003). Impaired wood quality is more sensitive to low B supply than leaf or shoot growth in plantation eucalypts (Dell *et al.*, 2001). Dell *et al.* (2006) reported Cu deficiency in bluegum plantations in south-western Australia, where *ca.* 200,000 ha of agricultural land have recently been turned over from annual pasture and crop production to plantations of fast-growing bluegum. Although soil residual Cu values were adequate for farming following application of Cu fertilisers over the previous three decades, Cu deficiency has emerged as a serious problem leading to poor bole form and reduced tree growth (Dell *et al.*, 2003).

In most cases, there was no or little response to NPK fertilisers at planting and Cu was the primary nutrient limiting establishment. Preliminary work suggests that Cu may be less available to bluegum than to annual crop/pasture species due to the main growth flush occurring in summer when root activity in the 0-15 cm soil horizon is curtailed by drought. Furthermore, bluegum produces more biomass than the crops it replaces. Not only does this place a greater demand on soil Cu pools, but compared to wheat there is greater export of Cu in wood (25-30 g Cu/ha/yr) than in grain (3.5–7.0 g Cu/ha/yr). This example highlights the need for more research on the requirement for micronutrients in emerging industrial plantation species.

The demand for micronutrients in plantation forests presents challenges for fertiliser strategies. At rates of B fertiliser that avoid B toxicity at planting of eucalyptus trees, B-deficiency symptoms may re-appear within 2-4 years of sowing (Dell *et al.*, 2001). The high biomass and sequestration of B in wood accounts for why the initial B fertiliser application fails to supply sufficient B after 2-4 years. The solution to this paradox is to either introduce topdressing of micronutrients in the established plantation, which is uncommon practice in forestry at present, or the use of slow-release B forms such as ulexite that can be applied at higher rates at sowing without inducing B toxicity.

Seed quality

Seed quality is sensitive to low micronutrient supply from the soil. Low Zn, Mn, Mo and B levels in particular decrease seed vigour (Welch, 1999). High Mo levels in seed can supply sufficient Mo to provide all the plant's requirements for growth to maturity (Harris *et al.*, 1965). In these cases, high Mo levels in seed for sowing are sufficient to avoid deficiency during crop growth on low-Mo soils. Similarly, seed with high Co content (0.73 mg/kg) can supply the plant's entire Co need to maturity even on low Co soils (Robson and Mead, 1980). At < 0.4 mg Co/kg of seed, Co responses by narrow-leaf lupin on low-Co soils increased with decreases in seed Co (Robson and Snowball, 1987).

In the case of Zn, B and Mn, the amounts of the micronutrient are rarely sufficient to supply the plant requirements to maturity but, nevertheless, low seed levels may impair seed quality and vigour and can eventually lower crop yield. Low B in seed decreases germination by decreasing seed viability (Bell *et al.*, 1989; Rerkasem *et al.*, 1997). For black gram, B concentrations < 6 mg/kg decreased germination while, for soybean, concentrations < 7-10 mg/kg decreased germination. Hence, if the level of B supply to the developing seed embryo is insufficient, irreversible damage to the embryo tissue occurs (Rerkasem *et al.*, 1997). Low seed Mn (7 mg/kg) has also been reported to decrease seed viability of narrow-leaf lupin (Crosbie *et al.*, 1993).

At levels of seed Mn and B that do not affect germination, seedling vigour may be still impaired (Bell *et al.*, 1989 ; Rerkasem *et al.*, 1993; 1997 ; Crosbie *et al.*, 1994). In the case of black gram, seeds containing between 6 and 20 mg B/kg produced seedlings that had abnormal shoot or root growth and decreased emergence (Bell *et al.*, 1989; Rerkasem *et al.*, 1993; 1997). The decrease in seedling vigour was most evident when seed was sown into low-B soils. At seed B > 20 mg/kg in the legumes, there was no evidence of impaired seed germination or vigour, even on low-B soil. In narrow-leaf lupin seed, increasing seed Mn from 8 to 55 mg/kg increased seedling growth in solution without added Mn, but not when external Mn was adequate (Crosbie *et al.,* 1994). In soil, seed Mn < 7 mg/kg depressed emergence and seed with 11 mg/kg or less had an increased percentage of abnormal seedlings (Longnecker *et al.*, 1996). Increased soil Mn supply did not overcome the detrimental effects of sowing seeds with 11 mg Mn/kg or less.

Similarly, with low seed Zn, seed vigour of wheat is impaired (Rengel and Graham, 1995; Yilmaz *et al.*, 1998). Even with the small seeded canola, increases in seed Zn resulted in greater seedling vigour and early growth on low-Zn soils (Grewal and Graham, 1997). In Zn-deficient areas of Central Anatolia, Turkey, low seedling vigour has led farmers to use seed rates for sowing wheat that are three times higher than recommended (Braun, 1999). The higher rates of seed are used to compensate for lower emergence and increased seedling death during winter. It is estimated that the use of seed with higher Zn would overcome the need for high seed rates and, in doing so, it would save 500,000 tonnes of seed per year. The economic benefit from seed saving in Central Anatolia, was estimated to be US$100 million per annum.

Where it is not possible to easily identify seed that is high in micronutrients for planting, seed treatment with micronutrient solutions to enhance micronutrient content has been beneficial in the case of Zn and Mo. Harris *et al.* (2007) showed that adding Zn to maize seed in priming solutions applied before sowing, increased seedling growth and eventually grain yield. The combined effect of priming and Zn addition increased maize grain yield from 3 to 3.8 t/ha. Seed application of Zn in priming solution had a 16-fold greater benefit:cost ratio than soil Zn application. Seed priming used a 1 % zinc sulphate ($ZnSO_4$) solution and priming lasted for 16 h.

Seed Mo treatment is practised in Bangladesh with sowing chickpea on clayey soils of the High Barind Tract that have acidic topsoils but neutral to alkaline sub-soils (Johansen *et al.*, 2007). On soils with topsoil pH (1:2; soil:H_2O) < 6, seed application of Mo increased nodulation of chickpea by 37-90 % and was as effective as soil Mo application. Only 13 g Mo/ha was applied with seed priming compared to soil application of 500 g Mo/ha. Seed Mo treatment increased nodulation and alleviated N deficiency in chickpea. If soil *Rhizobium* levels were low, both Mo and *Rhizobium* were needed with seed priming to achieve maximum crop yield. The approximate benefit:cost ratio from using Mo and *Rhizobium* peat inoculum with seed priming was 5 (Johansen *et al.*, 2007). An alternative approach that has been tried is to boost micronutrient levels in seeds before harvest. In rice, researchers in Bangladesh have shown that micronutrient enrichment of seed by multiple foliar applications to crops before harvest can boost yields of the next season's crops, largely by increasing seed Zn and Mo. Similar benefits were obtained from micronutrient enrichment of wheat seed (J. Lauren, personal communication). Except for Mo, sowing micronutrient-primed seeds is unlikely to result in enrichment of the progeny (Johnson *et al.*, 2005).

Disease resistance

One of the lesser known benefits of adequate micronutrient levels in plants is to decrease the severity of diseases. Microorganisms are sensitive to much lower concentrations of Cu, Mn and Zn than higher plants. Hence, salts of these metals have been used in various disease control products for a long time. Copper is used as a fungicide to control the growth of leaf pathogens such as mildew. A comprehensive review of this topic can be found in Graham and Webb (1991) who reported that severity of a number of root and shoot diseases is increased by micronutrient deficiencies. Foliar application of micronutrients (B, Mn, Zn) may also reduce the severity of foliar disease, such as tan spot in wheat (Simoglou and Dordas, 2006).

Under Zn deficiency, cell membranes become leaky and release organic compounds, which attract pathogens to the rhizosphere (Cakmak and Marschner, 1988). Zinc has been shown to suppress root-rotting pathogens, root nematode infestation and take-all infections (Brennan, 1992a; Rengel, 1997; Streeter *et al.*, 2001; Siddiqui *et al.*, 2002), possibly by reducing exudation of organic compounds from roots to the rhizosphere.

In wheat, Zn deficiency decreased resistance to *Fusarium graminearum* (Sparrow and Graham, 1988) and to *Rhizoctonia solani* (Thongbai *et al.*, 1993).

Wood and Robson (1984) reported that Cu deficient wheat plants were more severely affected by take–all fungus than Cu adequate plants. The take-all disease is suppressed by adequate Mn supply to wheat. Boron application has been effective in suppressing a number of fungal diseases (Graham and Webb, 1991; Stangoulis and Graham, 2007).

Some recent evidence of a beneficial role of B in disease suppression includes a reduction of *Xanthomonas campestris* pv. *Campestris* in caulifower (Kumar and Sharma, 1997) and a reduction of the pathogenic fungus *Plasmodiophora brassicae* Wor in *Brassica* species (Dixon, 1996). In addition, there is evidence that the efficacy of fungicides can be enhanced by application with B, although the mechanism remains unclear (Nott *et al.*, 1999). There is uncertainty about how B suppresses disease, but Stangoulis and Graham (2007) point first to a role of B in lignification and phenol metabolism as both are intrinsically associated with plant defence systems and, secondly, to the role of B as a structural component of the cell wall where it strengthens the barrier to suppress pathogen infiltration.

Chilling and freezing injury

There is some indication that B can play a protective role in preventing cold stress in warm-season crops (Huang *et al.*, 2005) and in increasing winter hardiness of cold climate species (Shorrocks, 1997). A link between B deficiency and leaf damage at low temperature in warm-season crop plants is suggested in field observations and glasshouse studies, but causal relationships between these two stresses have yet to be demonstrated. According to Huang *et al.* (2005), 'limited evidence at the whole plant level suggests that chilling temperature in the root zone restricts B uptake capacity and/or B distribution/ utilisation efficiency in the shoot, but the nature of this interaction depends on chilling tolerance of species concerned, the mode of low temperature treatment (abrupt *vs* gradual temperature decline) and growth conditions (e.g. photon flux density and relative humidity) that may exacerbate chilling stress.' In subtropical/tropical species such as cucumber, cassava and sunflower, root chilling at 10-17 ^{o}C decreases B uptake efficiency and B utilisation in the shoot and increases the shoot to root ratio, all of which can induce B deficiency when external B supply is marginal. Chilling-tolerant temperate species (e.g. oilseed rape, wheat) have a much lower threshold root chill temperature (2-5 ^{o}C) to induce B responses.

Boron deficiency in warm season crops exacerbates chilling injuries in leaf tissues, particularly under high photon flux density, with a number of possible mechanisms suggested (Huang *et al.*, 2005). However, specific evidence for each of the mechanisms is still lacking. Impacts of B status on chilling tolerance in crop species have important implications for the management of B during sensitive stages of growth, such as early establishment after planting and early reproductive development, both of which can coincide with the occurrence of chilling temperature in the field.

In the case of winter hardiness, there is some field evidence suggesting that B sprays protect shoots from frost damage (Braekke, 1979) and, that on low-B soils, trees are more sensitive to dieback (Beltram, 1958). However, until the study reported by Raïsänen *et al.* (2007), there was no clear experimental evidence backing either of these propositions. In Norway spruce (*Picea abies*), plants raised under low soil B had decreased cold acclimation in shoots and roots and decreased dessication tolerance. Therefore, it was concluded that susceptibility to freezing damage was increased by B deficiency in Norway spruce plants (Raïsänen *et al.*, 2007).

Human health

Improvements in human health also flow from the use of micronutrient fertilisers. Over 3 billion people suffer from micronutrient malnutrition globally (Welch, 2001). A large proportion of these cases should be treatable with greater use of micronutrient fertilisers. Yilmaz *et al.* (1997) report that large increases in grain Zn are obtained from foliar application of Zn to wheat, with the greatest benefits from application after the milk stage of grain development. However, despite the obvious potential for benefit to human health from micronutrient fertiliser application, there are few case studies where the benefit has been quantified.

An indicative example is the enrichment of NPK fertilisers in Finland with selenium (Se) (Cakmak, 2008c). Selenium is an important constituent of anti-carcinogenic compounds that prevent development of cardiovascular diseases and improve the human immune system (Combs and Gray, 1998; Rayman, 2005). Selenium was low in the diets of many people in Finland due to low soil Se levels and, consequently, low Se in cereal grains. In order to provide the health benefits from increased Se intake in the diet to most of the population, the government of Finland implemented a mandatory programme of enrichment of NPK fertilisers with 16 mg Se/kg. From 1984 to 1985, following the introduction of Se-enriched fertilisers, Se intake in Finland increased from 35 μg/ person to 110 μg/person. Subsequently, Se enrichment of NPK fertilisers has been reduced to 10 mg Se/kg in order to ensure that human intake reached the target level of about 70 μg Se/person without risk of excess.

Additional reading

Alloway, B.J. (ed.) (2008c). *Micronutrient Deficiencies in Global Crop Production*. Springer, Dordrecht.

Fageria, N.K., Baligar, V.C. and Clark, R.B. (2002). Micronutrients in crop production. Advances in Agronomy 77: 185-268.

Graham, R.D. (2008). Micronutrient deficiencies in crops and their global significance. p. 41-61. In B.G. Alloway (ed). *Micronutrient Deficiencies in Global Crop Production*. Springer, Dordrecht.

Welch, R.M and Graham, R.D. (2005). Agriculture: the real nexus for enhancing bioavailable micronutrients in food crops. Journal of Trace Elements in Medicine and Biology, 18: 299-307.

5. Types of micronutrient fertiliser products: advantages and disadvantages of the different types

There is a diverse array of micronutrient fertilisers in the world, ranging from straight micronutrient fertilisers to blends with straight macronutrient fertilisers and micronutrients incorporated into compound fertilisers. Both liquid and solid forms are available and formulations have been developed for foliar and/or soil application.

Chemical and physical nature of products

Straight micronutrient products

The main inorganic sources of micronutrients for the fertiliser industry include metallic salts (e.g. chlorides, nitrates, sulphates), borates, carbonates, molybdates and oxides (Table 5.1).

Boron fertilisers are available as either crushed ores or refined products. The refined products, mainly borax (sodium tetraborate) and boric acid, are available in powdered or granular forms and are suitable for soil or foliar application. These sources are readily soluble and available for plant uptake. Three forms of borax are available, differing in hydration, giving rise to varying solubility, although the differences have little agronomic significance. Solubor® ($Na_2B_8O_{13}.4H_2O$) was developed for use as a foliar fertiliser. It is highly soluble in water and readily forms supersaturated solutions. It is considered to be a hybrid between borax and boric acid, but is more soluble than either of them. Crushed B ores, particularly colemanite and ulexite have been used as B fertilisers. The ores can be slightly less soluble than the refined products due to the ore composition and amount of insoluble material, which varies with source. Uncertainty about the availability of B from ores has restricted their use for annual species.

The metallic cations (Cu, Fe, Mn and Zn) are available as oxides, carbonates and salts, such as sulphates, nitrates and chlorides. The sulphates are the most commonly used micronutrient sources, being highly soluble and suitable for soil and foliar application. Sulphates are available in crystalline and granular forms. The popularity of sulphates is due to their relative effectiveness, low cost, wide availability and ease of handling. The chlorides and nitrates of Cu, Fe, Mn and Zn are often used in liquid fertilisers. The oxides are cheaper per unit metal than the sulphates but are insoluble.

The immediate effectiveness of oxides can be low and, to be effective over time, they should be evenly applied and mixed into the soil to maximise soil contact. They can be ineffective when applied in a granular form. Oxysulphates are oxides of Cu, Mn and Zn partially acidulated with sulphuric acid (H_2SO_4). The water solubility of the micronutrient is directly related to the degree of acidulation. Several studies have published results showing that the effectiveness of granular Zn oxysulphates is related to their water solubility. It has been recommended that the water-soluble Zn content be above 40-50 % of the total Zn to be effective at supplying Zn (Gangloff *et al.*, 2002; Slaton *et al.*, 2005). In a few countries, metal slags are used as a source of micronutrients, particularly Cu.

The most commonly used compounds for Mo fertilisers are ammonium and sodium molybdates and molybdenum trioxide. The molybdates are soluble, and can be used in foliar sprays. When applied to the soil, Mo fertilisers are generally combined with NPK fertilisers or with the seed because of difficulties in applying the very small amounts of Mo required in crop production.

Table 5.1. Inorganic sources of micronutrients for the fertiliser industry.

Compound	Formula	Element content (%)	Water solubility
Boron - *refined products*			
Boric acid	H_3BO_3	17.5	Soluble
Sodium pentaborate	$Na_2B_{10}O_{16}.10H_2O$	18	Soluble
Sodium tetraborate (Fertibor®)	$Na_2B_4O_7$	21	Soluble
Sodium tetraborate pentahydrate (borate)	$Na_2B_4O_7.5H_2O$	15	Soluble
Sodium tetraborate decahydrate (borax)	$Na_2B_4O_7.10H_2O$	11	Soluble
Disodium octaborate tetrahydrate (Solubor®)	$Na_2B_8O_{13}.4H_2O$	21	Soluble
Boron - *crushed ores*			
Ascharite	$2MgO.B_2O_3.H_2O$	variable	Slightly soluble
Colemanite	$2CaO.3B_2O_3.5H_2O$	variable	Soluble
Datolite	$2CaO.B_2O_3.2SiO_2.H_2O$	variable	Slightly soluble
Hydroboracite	$CaO.MgO.3B_2O_3.6H_2O$	variable	Slightly soluble
Ulexite	$Na_2O.2CaO.5B_2O_3.16H_2O$	variable	Soluble
Copper			
Copper chloride	$CuCl_2$	47	Soluble
Copper hydroxide	$Cu(OH)_2$	25	Soluble
Copper oxychloride	$3Cu(OH)_2.CuCl_2$	25	Soluble
Copper sulphate monohydrate	$CuSO_4.H_2O$	35	Soluble
Copper sulphate pentahydrate	$CuSO_4.5H_2O$	25	Soluble
Cuprous oxide	Cu_2O	89	Sparingly soluble
Cupric ammonium phosphate	$Cu(NH_4)PO_4.H_2O$	32	Soluble

Iron			
Ferrous ammonium phosphate	$Fe(NH_4)PO_4.H_2O$	29	Soluble
Ferrous ammonium sulphate	$Fe(NH_4)_2(SO_4)_2.6H_2O$	14	Soluble
Ferrous sulphate (monohydrate)	$FeSO_4.H_2O$	33	Soluble
Ferrous sulphate (heptahydrate)	$FeSO_4.7H_2O$	19.5	Soluble
Ferric ammonium citrate	$C_6H_8O_7.xFe.xNH_3$	14-19	Soluble
Ferric sulphate	$Fe_2(SO_4)_3.9H_2O$	20	Soluble
Manganese			
Manganese carbonate	$MnCO_3$	47	Sparingly soluble
Manganese chloride	$MnCl_2$	44	Soluble
Manganous oxide	MnO	77	Insoluble
Manganese dioxide	MnO_2	63	Insoluble
Manganese oxysulphate	$xMnSO_4.xMnO$	30-50	Variable
Manganese sulphate	$MnSO_4.xH_2O$	23-32	Soluble
Molybdenum			
Ammonium molybdate	$(NH_4)_6Mo_7O_{24}.4H_2O$	54	Soluble
Molybdenum trioxide	MoO_3	60	Slightly soluble
Molybdic acid	$H_2MoO_4.H_2O$	20-30	Soluble
Sodium molybdate	$Na_2MoO_4.2H_2O$	53	Soluble
Zinc			
Ammoniated zinc sulphate	$Zn(NH_3)_4SO_4$	10	Soluble
Basic zinc sulphate	$ZnSO_4.4Zn(OH)_2$	55	Slightly soluble
Zinc carbonate	$ZnCO_3$	50-56	Insoluble
Zinc chloride	$ZnCl_2$	47-50	Soluble
Zinc nitrate	$Zn(NO_3)_2.3H_2O$	22	Soluble
Zinc oxide	ZnO	50-80	Sparingly soluble
Zinc oxysulphate	$xZnSO_4.xZnO$	20-60	Variable
Zinc sulphate heptahydrate	$ZnSO_4.7H_2O$	22-23	Soluble
Zinc sulphate monohydrate	$ZnSO_4.H_2O$	36-37	Soluble

The term “sparingly soluble” means that the product is not totally insoluble, particularly when present in small particle sizes (with a large surface area). This terminology reflects recent technological advances in micronutrient product formulation (Moran, 2004).

NPK fertilisers with micronutrients

Because the recommended application rate for micronutrients is generally less than 10 kg/ha, it can be difficult to achieve a uniform application in the field using conventional equipment. As a result, NPK fertilisers are commonly applied simultaneously, acting as carriers for the micronutrients. Also, by combining micronutrient application with NPK fertilisers, the need for separate applications is eliminated, thus reducing handling costs.

Micronutrients can be combined with NPK fertilisers by dry mixing, bulk blending granular fertilisers, coating micronutrients onto granular NPKs, incorporating micronutrients during manufacture or by mixing with fluid fertiliser. Dry mixing involves simply combining dry micronutrient material with macronutrient sources. When produced using granular material, it is generally referred to as bulk blending. Dry mixing of non-granular materials is becoming less common.

Dry mixing and bulk blending can be done in small batches allowing the creation of specially tailored fertiliser to meet the needs of individual farmers or fields. Also, blends can be made just prior to application, reducing the need for extra storage space and reducing the chance of chemical reaction between the fertiliser components. Dry mixing fine materials (< 1 mm) avoids the problem of segregation, which is a serious issue for bulk blended fertilisers. However, fine materials can lead to dust problems and are more susceptible to caking, which can be exacerbated by the use of hygroscopic micronutrient sources (e.g. $ZnSO_4.7H_2O$, $CuSO_4.5H_2O$). These micronutrient sources can cause similar problems for granular fertilisers.

Bulk blending is more popular because of the convenience and wide utilisation of granular fertilisers. The main problem with including micronutrients via bulk blending with NPK products is segregation of the different components during blending, transportation and application. The major cause of segregation is a difference in particle size among the fertiliser components. Segregation can be minimised by closely matching the particle size of the micronutrient and NPK sources. Various mechanical means have been developed to minimise segregation during handling and storage.

Due to the relatively small amounts of micronutrients required compared to macronutrients, bulk blending of granular material can result in a sparse distribution of micronutrient granules in the field. For example, when $ZnSO_4$ is applied at a rate of 1 kg/ha, the number of granules per unit area may be less than $20/m^2$. The distribution is reduced with increasing granule size and the concentration of the micronutrient source. This problem can be reduced by using an inert carrier for the micronutrient material or by using a primary nutrient as a carrier. Granular macronutrient products are available with higher micronutrient content for the purpose of bulk blending.

Incorporating micronutrients during the manufacture of granular fertilisers that contain primary nutrients results in a uniform distribution of nutrients in each granule. However, due to the large scale of granulation plants, it is uneconomical to produce small tailor-made batches. Micronutrients are generally only incorporated during the manufacture of NPKs where there is a large regional demand. For example, in parts of Australia, large areas of pasture and field crops require amendment with Zn, Cu and Mo. Here, farmers have access to a variety of fertilisers, including superphosphate and NPK formulations that contain one or more micronutrients.

The manufacture of compound micronutrient fertiliser involves combining micro- and macronutrient materials under conditions of high temperature and moisture. As a result, chemical reactions occur, and these reactions can alter the availability of the micronutrients. Soluble salts of Cu, Mn, Fe and Zn become partially insoluble when incorporated with ammonium orthophosphates, presumably through the formation of metal ammonium phosphates such as $ZnNH_4PO_4$ (Hignett and McClellan, 1985). Loss of solubility reduces the immediate plant availability of the nutrients, but the residual value may be similar to straight sources (Mortvedt, 1991). Polyphosphates and superphosphates, on the other hand, may increase the solubility of insoluble micronutrient sources such as the oxides and carbonates. The timing of application of the micronutrient into the manufacturing process may influence the effectiveness of the micronutrient. For example, ZnEDTA is best incorporated into superphosphate with the ammonifying solution, to avoid decomposition of the organic ligand.

Micronutrients can be coated onto the surface of NPK granules using a binding agent. Binding agents often used include water, oils, waxes and other fertiliser solutions. Water and fertiliser solutions achieve adherence through chemical bonds whereas oils and waxes provide a mechanical bond. Fertiliser solutions such as APP (ammonium polyphosphate) and UAN (urea ammonium nitrate) can be used to provide adherence without the loss of analysis that accompanies some binding agents. The choice of the binding agent is important, as a poor binding agent can result in separation of the micronutrient from the granule, leading to segregation, or it may increase the chance of caking during storage.

Coating with micronutrients allows the flexibility to produce individually tailored fertilisers in small batches, similar to bulk blending, with the advantage of a uniform application as with a compound fertiliser. Efficacy of the micronutrient should be similar to when it is incorporated during manufacture because of reactions between the fertiliser components. One of the disadvantages is the additional production costs, which limit the use of this process mainly to premium fertilisers.

Liquid mixes

Fluid fertilisers are gaining popularity as an alternative to granular NPK products. Micronutrients can be incorporated with fluid fertilisers, which provides a convenient and uniform method of application. However, it is important to select compatible micro- and macronutrient sources. For example, the solubility of most micronutrient sources in UAN (urea ammonium nitrate) is low: the solubility of $ZnSO_4.H_2O$ and $Fe(NO_3)_3.9H_2O$ are only 0.5 %. If the pH is maintained between 7 and 8 with NH_4^+, the solubility of $ZnSO_4$ increases to 2 %, allowing more practical rates for application (Silverberg *et al.*, 1972). Solubility of Cu, Fe, Mn and Zn is greater in polyphosphate solutions than in orthophosphate solutions, as the polyphosphates sequester the metallic micronutrients allowing them to maintain higher levels in solution. This property, however, does not translate to greater efficacy once applied, as polyphosphates are quickly hydrolysed within the soil. Fluid forms of P, such as APP, have been found to be more agronomically efficient than granular forms of P on calcareous soils (McBeath *et al.*, 2005), and these soils often are deficient in micronutrients such as Zn, Mn and B.

A more recent development in micronutrients for foliar application is the formulation of suspension concentrates. These are fluids in which the solubility of component micronutrients has been exceeded and clay has been added to keep the fine, undissolved fertiliser particles from settling out (Moran, 2006).

Chelated and enhanced micronutrients

Chelated and enhanced micronutrients are a group of products in which the micronutrient source is bound to an organic ligand in order to improve its availability to plants. These products include natural and synthetic chelates and natural organic complexes (Table 5.2). The technology was originally applied to the correction of Fe deficiency in calcareous soils.

Table 5.2. Chelated forms of micronutrients and some other organic complexes used as fertiliser.

Product	Formula	Element content (%)
Copper chelates	$Na_2CuEDTA$	13-14
	NaCuHEDTA	9
Copper lignosulphonate		4-5
Copper polyflavonoid		4-7
Iron chelates	NaFeEDTA	5-14
	NaFeHEDTA	5-9
	NaFeEDDHA	4-6
	FeEDDHMA	4-6
	FeEDDHSA	3-6
	NaFeDTPA	10
	FeEDDCHA	6
Iron lignosulphonate		5-8
Iron polyflavonoid		9-10
Manganese chelates	MnEDTA	5-12
	MnDTPA	6
Manganese lignosulphonate		5
Manganese polyflavonoid		5-8
Zinc chelates	$Na_2ZnEDTA$	8-14
	NaZnHEDTA	6-10
	NaZnEDTA	9-13
	NaZnNTA	9-13
Zinc lignosulphonate		5-12
Zinc polyflavonoid		5-10

A chelate uses a series of coordinate bonds to combine with a metal forming a relatively stable cyclic structure. The word chelate is derived from the Greek word 'chela' meaning 'claw', which describes the chemical structure of the resulting 'chelation complex'. The chelate surrounds the metal, preventing it from reacting with the soil, thus maintaining it in a plant-available form that crop roots can access. The efficacy of a particular metal-chelate complex is largely determined by its stability constant: a measure of its ability to hold the micronutrient in the chelated form against substitution by competing cations (Mortvedt, 1991).

The most commonly used synthetic chelate for micronutrient fertilisers is EDTA (ethylenediamine tetraacetic acid). For soil applications of Fe, other N-carboxylalkyl-amino acid chelates, mainly EDDHA (ethylenediamine di(o-hydroxyphenylacetic acid) and HEDTA (hydroxyethyl-ethylenediamine triacetic acid) are more effective, depending on soil pH. Impurities within Fe chelates, particularly EDDHA, has been a problem in the past, resulting in Fe values on the label often exaggerating the Fe content of the fertiliser (Lucena, 2003). New chelates being evaluated as fertilisers include $EDDH_4MA$ (ethylenediamine-bis(2-hydroxy-4-methylphenyl)acetic acid) and PDDHA (propylenediamine-N,N'-bis(o-hydroxyphenyl)acetic acid).

Natural organic complexes are a diverse group of products formed by reacting metallic salts with organic by-products (e.g. from the wood pulp industry). Organic complexes are often marketed as 'organic chelates', but there is little evidence that they have a true chelate structure or property. The chemical structure of organic complexes has not been well defined and may vary considerably according to the processes used in their manufacture. As a result, it is not possible to define their stability constants. However, it is presumed that they would be lower than those of the synthetic micronutrient chelates (Mortvedt, 1991). In the industry, there are many claims regarding the relative efficiency of natural organic complexes compared with the mainstream micronutrient sources (synthetic chelates and inorganic sources). Claims that organic complexes are up to 10 times more effective than inorganic sources have not been confirmed independently in published studies. Scientific research has found that true synthetic chelates can be up to 3 to 5 times more effective than organic sources in some applications.

While chelated and enhanced micronutrients may be more effective per unit micronutrient at supplying micronutrients, they are also more expensive. The price of these products generally limits their use to higher value crops, such as horticultural crops. In many cases, it is more cost effective to apply inorganic sources at higher rates. Some products contain a combination of synthetic chelates and organic complexes in order to reduce costs, but presumably the effectiveness is also reduced. Their effectiveness in foliar applications is considered in Chapter 6.

Fritted and slow-release products

Slow-release products have been suggested (Mortvedt, 1994) as a method of increasing fertiliser efficiency by providing an adequate supply of nutrients for the plant, whilst minimising the loss of nutrients via leaching or by immobilisation by the soil. However, there is only a limited range of useful products available. Frits are manufactured by fusing one or more powdered micronutrient sources with silicates in a furnace at about

1350°C to produce a vitrified homogeneous material that is ground into a powder. The slow weathering of the silicates limits the release of the micronutrients, which can be regulated by the fineness of grinding and the inclusion of impurities such as Ca, Na, K and Al into the silicate matrix (Fleming, 1980). Powdered frits can be granulated and incorporated during the manufacture of NPK fertilisers, or they can be coated onto the granule surfaces. Frits were designed for use on coarse-textured soils in high rainfall areas where leaching of soluble micronutrient sources is a problem. Their slow availability means that frits are better suited to maintenance applications rather than for correcting deficiencies. Hence, agricultural use of frits is limited, but they remain of interest in horticulture.

The majority of B fertilisers are highly water soluble and can readily leach from the soil in high rainfall areas. Some growers have experienced toxic rates of B applied at planting of perennial crops, followed within a few years by the appearance of B deficiency. The supply characteristics of frits or B ores are not sufficiently robust to deliver the B requirement of many crops under leaching conditions or in soils of low-B supply. New granular slow-release B products are being designed to meet this challenge (Flores *et al.*, 2006). The slow-release properties are developed through varying blends of different B ores, particle size and hardening temperatures. By contrast, the relatively long residual values of most Zn and Cu fertilisers (Chapter 7) reduce the need for slow-release products of these elements.

Efficacy comparison: uptake via foliage, uptake from soil

Plants can take up micronutrients from the soil solution and by foliar absorption. However, whereas uptake by roots guarantees delivery of micronutrients to all parts of the plant, uptake by leaves has limitations. Thus, foliar fertilisation may not be sufficient to supply the long-term demand for crop growth. Therefore, it should be considered as supplementary to soil application. Neumann (2004) concluded that "batch applications of foliar micro- or macronutrients, alone or in combination, will nearly always be a less effective option than application of nutrients to the soil for uptake by the root". Nevertheless, foliar fertilisation with micronutrients is an important tool and, if properly targeted, it can be effective in delivering nutrients to the crop at critical stages in its growth (Chapter 6).

Examples where foliar applications are recommended:

- to rescue micronutrient deficiency in the current crop;
- to prevent micronutrient deficiency in the current crop where soil application is unlikely to be effective (e.g. dry soil, calcareous soil) or is operationally difficult (e.g. applying small amounts of Mo to legume pastures); and
- in the biofortification of cereals and grain legumes.

There is much greater variation in leaf than root traits in plants, and this may affect nutrient acquisition by crops. Foliar fertilisation rates must take into account the ability of the micronutrient ion or compound to adhere to and penetrate into the leaf surface. The variation in leaf characteristics among crops can partly be overcome by the use of chemical additives such as surfactants, adjuvants and penetrants (Chapter 6). Once inside the leaf, the micronutrient is only effective if it can reach the target tissue. New organs such as leaves and flowers that form after the spray event rely on the internal transport of the sprayed micronutrient. Unfortunately, not all micronutrients are able to be transported to the site of need. In the case of B, some species such as apples and lupins can redistribute B that is foliar applied, but most species cannot. Therefore, foliar application of B is likely to have restricted application in many crops.

In contrast to foliar application of micronutrients, the addition of micronutrients to soil not only benefits the current crop, but some residual fertiliser is available to support future cropping cycles, often for 10-25 years. Also, higher rates of micronutrients can be used without the risk of causing toxicity. The exception to this is B, which has a relatively narrow range between deficiency and toxicity. Apart from Fe, the uptake of micronutrients from soils is generally not problematic, provided the micronutrients are present in the soil horizon where root activity is high and uptake can occur when the internal demand for growth is high.

The type of micronutrient fertiliser to use in soil is an important consideration for the current crop as micronutrient supply constraints can impair early seedling development. For example, increasing the water-soluble Zn content of the fertiliser (Gangloff *et al.*, 2002) and decreasing particle size appear to be important for early nutrient uptake. Slaton *et al.* (2005) showed that the choice of Zn fertiliser was critical for the yield of rice gown in the same year that fertiliser was applied, but that the residual benefits of Zn fertilisation were affected only by application rate.

Another factor affecting the efficacy of uptake of micronutrients from soil-applied fertiliser is fertiliser placement. Banding can be effective in reducing soil chemical reactions with Mn, Cu and Fe-containing fertilisers that limit the availability of micronutrients in the soil solution.

Field studies in Central Anatolia, Turkey show that application of Zn fertiliser can enhance the grain Zn concentration of wheat up to 3-fold (Yilmaz *et al.*, 1997). The best strategy for achieving this is a combination of soil and foliar applied Zn (Table 5.3). Since Zn deficiency is a global risk factor for human health (Hotz and Brown, 2004), these findings provide an opportunity to biofortify cereal grains, whilst breeders search for traits associated with micronutrient dense grains.

With regard to B fertilisation, foliar application can enhance yield, especially if applied at the time of critical demand for vegetative and reproductive growth. However, due to differences in the nutritional physiology of crop species, a cost-benefit analysis may need to be undertaken for soil *vs* foliar fertilisation for each crop type.

Table 5.3. Effect of Zn application method on grain yield and grain Zn concentration averaged for one durum and three bread wheat cultivars grown in Zn-deficient soil in Central Anatolia, Turkey (Yilmaz *et al.*, 1997). The grain yield for control (without Zn) plants was 558 kg/ha.

Zn application method	Grain yield (% increase)	Grain Zn (mg/kg)
Control	-	10
Soil	265	18
Seed	204	10
Foliar	124	27
Soil + foliar	250	35
Seed + foliar	268	29

Appropriateness for different crop types

Generally, there is little if any discrimination of micronutrient fertiliser form by crop species. Except for B, which can be taken up as undissociated boric acid, roots can only absorb micronutrients as ions in soil solution or coupled to carrier compounds such as phytosiderophores. However, the amount of the micronutrient taken and utilized for growth can differ significantly among crops. Crops can be classified into categories depending on their micronutrient requirement, e.g. high requirement for B in mustard and sugar-beet, low requirement for B in potato and rice, high requirement for Zn in maize, and so on. Because of the nature of their cell walls, broadleaf crops generally have a higher requirement for B than grasses. However, because B is necessary in cereals for pollen fertility, the availability of B at flowering is critical, and the impact of the timing of a small amount of B fertiliser on reproductive yield can be substantial.

Other factors affecting the magnitude of the micronutrient fertiliser requirement include: the amount of nutrient removed off-site in the harvest, the crop rotation practice, the extent of erosion and loss through leaching, and the micronutrient efficiency of the genotype. Nutrient efficiency can result from more effective nutrient capture, transport and utilization. In conclusion, micronutrient fertilisers should be chosen for their cost effectiveness in increasing yield or quality of the present crop and sustaining productivity into the future. Nutrient availability and longevity in the soil environment in relation to climate and agronomic practices are factors that may need to be considered.

Appropriateness for different production systems

Consideration should be given to micronutrient fertiliser selection and method of application in different cropping systems, depending on soil conditions. For example, deficiency of Fe for rice is more likely in upland soils than in irrigated or paddy rice, unless the latter soils are alkaline or calcareous (Dobermann and Fairhurst, 2000). The shift from flooded to aerobic rice is leading to an increase in Zn disorders in rice in China (Gao *et al.*, 2006). Thus, micronutrient fertiliser recommendations need to be responsive to changes in crop management practices.

The placement of micronutrient fertilisers in soil can affect their efficacy to meet the current demand for crop growth as well as future crops (residual effect). Concentrating the micronutrients either by banding, spot application or by drilling at the time of sowing can reduce the rate of some soil reactions and increase the effectiveness of fertiliser Fe and other elements in some soils. Where the moisture content of surface soils declines rapidly in the spring, as in areas with Mediterranean type climate, it may be advantageous to place Mn fertiliser at depth (20-30 cm) to ensure that roots can continue to access Mn during seed fill (Crabtree, 1999).

In calcareous soils, the availability of Fe, Zn and Mn is impaired in most crops, and special consideration must be given to how best to supply the elements to sustain yield. Fertilisers that can maintain the micronutrient content of the soil in a labile form are preferred. Synthetic Fe(III)-chelates are commonly used to supply Fe under these circumstances, particularly FeEDDHA and FeEDDHMA, because they are stable under neutral and alkaline soil conditions and can maintain Fe in soil solution for root uptake. More recently, it has been suggested that, due to reduced binding to soil surfaces, FeEDDHSA and FeEDDCHA should be used in soils having high amounts of oxides and organic matter (Álvarez-Fernández *et al.*, 2001; 2008).

Unless organic matter is applied at the same time, $FeSO_4$ is ineffective as the Fe is rapidly removed from the soil solution and thus is unavailable for uptake. By contrast, $MnSO_4$ can be effective in correcting Mn deficiency in cereals on calcareous soils. In a recent study in South Australia, the relative response to Zn and Mn was greater when they were mixed with a suspension fertiliser (DAP) than when applied as a granular coating (Holloway *et al.*, 2001; 2008).

There is a wide range of micronutrient products in the market place, and this can sometimes be confusing for growers. When selecting fertiliser types, consideration should be given to the likelihood that nutrients can be leached offsite due to rain or irrigation (B is particularly vulnerable). Controlled-release fertilisers can be advantageous under these conditions, especially in sandy soils.

The main factors to consider when choosing micronutrient products for fertigation and hydroponic systems are solubility and compatability. For example, if $Ca(NO_3)_2$ is present in the solution, then inorganic sulphates should be avoided. Chelated forms of Fe are recommended and FeEDDHA has greater stability than FeEDTA, especially above pH 6.5.

Comparison of relative costs and benefits

Selecting a micronutrient fertiliser requires consideration of cost, effectiveness of the micronutrient compound for the current crop and for future crops, as well as consideration of compatibility with other crop management practices. There are numerous studies that demonstrate the cost effectiveness of applying micronutrient fertilisers to increase grain yield, and a small number for grain quality. In addition to increase in yield, the value of the crop may be enhanced, e.g. through improved Zn content or availability in wheat, which has benefits for human nutrition (Chapter 3). The identification and correction of Zn deficiency in wheat in Turkey is a recent success story (Cakmak, 2004) and other examples are discussed in Chapter 4.

Iron-chelates are effective but their cost precludes their use in many parts of the world. Slow-release products have been suggested as a method of improving the efficacy of less expensive fertiliser sources such as $FeSO_4$, which is not efficient in many soils due to rapid precipitation of Fe to form Fe hydroxide. These approaches include banding $FeSO_4$ with hydrophyllic polyacrylamide gels, developing S-coated Fe granules and immobilising Fe-chelates in sepharose gel. Some naturally occurring crystalline Fe products, for example vivianite ($Fe_3(PO_4)_2.8H_2O$) and pyrite (FeS_2), are more effective than $FeSO_4$ but of limited supply.

Low-stability synthetic Fe-complexes (e.g. with citrate, fulvates, lignosulphonates), which are intermediate in cost, can maintain Fe in the soil solution, but not in calcareous soils (Lucena, 2006). In conclusion, it may be more cost-effective to apply foliar Fe on a regular basis than to try to correct Fe deficiency in calcareous soils. Recently, Alvarez and Gonzalez (2006) have assessed the effectiveness of Zn complexes, and these data can be used in cost-benefit analyses of the different commercial products.

Often, there is much spatial heterogeneity in the occurrence of micronutrient constraints in the field. Precision farming should enable these areas to be treated economically. For example, Godsey *et al.* (2003) showed that Fe deficiency in irrigated maize was economical to correct if only responsive sites were treated using the optimal rate of 81 kg $FeSO_4.H_2O$ per hectare.

Environmental impacts

Decisions on rates, types, timing and frequency of application of micronutrient products need to consider environmental impacts, as well as the expected benefits from increased production or quality of agricultural and forestry products. Environmental impacts arising from adhering to recommended best practice for micronutrient use (Chapter 7) should be minimal and rare. Where environmental impacts arise, it will generally result from excessively high rates from single or repeated applications, from inadvertent or unplanned inputs of micronutrients carried in fungicides, recycled waste, or from co-contaminants or solvents used in the fertilisers (Mortvedt, 1996; Westfall *et al.*, 2005).

Micronutrient metals used as fertilisers or as additives in compound fertilisers may be sourced from industry by-products because of their lower cost (Mortvedt, 1985a; Mortvedt and Gilkes, 1993; Westfall *et al.*, 2005). By-products comprising dusts from galvanising processes, pigments, rubber and batteries are used as Zn sources (Mortvedt, 1985). However, industry by-products may contain variable levels of a range of metals (Table 5.4). For example, in a study by Mortvedt (1985b), several Zn fertilisers prepared from industrial by-products contained high levels of Cd, Ni and Pb, but not all were equally contaminated with the metals.

Table 5.4. Concentrations of cadmium (Cd), nickel (Ni) and lead (Pb) in Zn fertilisers applied to soil (Mortvedt, 1985b).

Zn fertiliser	Total Zn	Heavy metal concentration (mg/kg)		
	(g/kg)	Cd	Ni	Pb
$ZnSO_4$ (reagent)	275	1	1	1
$ZnSO_4$-1	340	2165	92	60
Zn oxysulphate-1	351	590	158	44000
Zn oxysulphate-2	415	1970	19	400
ZnO (reagent)	734	1	1	1
ZnO by-product-1	583	243	8950	1900
ZnO by-product-2	340	1420	250	5200

While it has been argued that minor amounts of heavy metals are added to soil as co-contaminants with micronutrient fertilisers, repeated applications may give rise to excessive loading. At an application rate of 10 kg/ha, the Zn micronutrient fertilisers in Table 5.4 will supply up to 22 g of Cd, 90 g of Ni and 440 g of Pb per hectare. In a soil that contained a background level of 0.15 to 1.5 kg Cd/ha (Westfall *et al.*, 2005), the highest loading of Cd would be equivalant to 15 % of the soil content, and it would double the soil Cd level if applied annually for 7 years. To avoid the inadvertent build-up of heavy metals in soils, in recent years, several countries have enacted regulations to limit the use of industry by-products as micronutrient fertiliser sources (Westfall *et al.*, 2005). In 1979, Canada established soil loading limits for phosphate and micronutrient fertilisers, which regulate the total amount of nine elements (As, Cd, Co, mercury (Hg), Mo, Ni, Pb, Se and Zn) that can be applied over a 45-year period (Table 5.5). Individual states of the USA also developed regulations that limited the application of heavy metals in fertilisers but, more recently, a national programme has been established by the Association for American Plant Food Control Officials (AAPFCO) to achieve uniform fertiliser regulations in all states. Current recommendations by AAPFCO (2006) list the maximum allowable concentrations of heavy metals in phosphate and micronutrient fertilisers. The loading is based on the overall rate of application of the plant nutrients in the fertiliser.

Table 5.5. Maximum allowable concentrations of elements in phosphate and micronutrient fertilisers suggested by Association for American Plant Food Control Officials for state regulations in the USA (Mortvedt, 1996).

Element	mg/kg of fertiliser per 1 % P_2O_5	mg/kg of fertiliser per 1 % micronutrient
Arsenic	13	112
Cadmium	10	83
Cobalt	3100	23000
Lead	61	463
Mercury	1	6
Molybdenum	42	300
Nickel	250	1900
Selenium	26	180
Zinc	420	2900

Additional reading

Alloway, B.J. (2008a). *Zinc in Soils and Crop Nutrition*, 2nd ed. IZA and IFA, Brussels and Paris.

Barton, L.L. and Abadia, J. (2006). *Iron Nutrition in Plants and Rhizospheric Microorganisms*. Springer, Dordrecht.

Dell, B., Brown, P.H. and Bell, R.W. (Eds) (1997). *Boron in Soils and Plants: Reviews*. Dev. in Plant and Soil Sciences Vol. 77. Kluwer Academic Press, Dordrecht.

Mortvedt, J.J., Cox, F.R., Shuman, L.M. and Welch, R.M. (Eds) (1991). *Micronutrients in Agriculture*, 2nd ed. SSSA Book series No.4. Soil Science Society of America, Madison, Wisconsin.

6. Application strategies

Micronutrient requirements for crops are usually met by the addition of micronutrient fertilisers to soil. As only small amounts are required, typically a few kg per ha, they are widely applied with macronutrient fertilisers (Mortvedt, 1991). This is not only convenient, but it ensures more uniform application (UNIDO and IFDC, 1998). However, in some parts of the world, micronutrients are still applied separately because farmers do not have access to specialty fertilisers due to the lack of manufacturing capacity to produce compound and blended fertilisers of high quality.

In horticulture, micronutrients are routinely supplied in the irrigation water or as foliar sprays. Foliar application is also the method of choice for some flood irrigated crops and non-irrigated field crops, including cereals and grain legumes. Useful reference information is available online in IFA's World Fertiliser Use Manual (**www.fertilizer.org/ifa/Home-Page/LIBRARY/World-Fertilizer-Use-Manual**) and in older publications (e.g. Martens and Westermann, 1991). In addition to specialty micronutrient fertilisers, it is worth noting that, depending on the source, rock phosphate may contain useful amounts of Zn and B. The purpose of this chapter is to provide the reader with an overview of the advantages and disadvantages of the different application strategies.

Fertiliser fortification

The addition of micronutrient compounds (Chapter 5) to macronutrient fertilisers provides farmers with various options for on-farm fertiliser management, and it can reduce the overall cost of applying micronutrient fertilisers. Firstly, more uniform distribution of micronutrients is possible in the field than if small amounts of micronutrient fertiliser were to be applied separately. Secondly, many crops will have an adequate supply of micronutrients throughout the crop cycle without the need for topdressing. Thirdly, a wide range of fertiliser composition and types can be produced suitable for different crops, soil types and delivery systems. Fourthly, the micronutrients can be broadcast, banded on the surface or at depth, drilled with the seed or incorporated into the soil. Experience differs in various regions of the world as to what method is more efficacious for the current and future crop cycles (e.g. Brennan, 1999b; Karamanos *et al.*, 2005). Local recommendations on rates and methods of application based on field experimentation should be followed.

When applied to the soil, most micronutrients do not need to be repeated on an annual basis as residual fertiliser is available for uptake by subsequent crops. The residual effectiveness varies with the element and soil type, ranging from one season in the case of B (Shorrocks, 1997) to several decades for Cu (Brennan, 2006). Exceptions occur however due to differences in the behaviour of micronutrients in soil and the limited availability of micronutrients in some soils, particularly those with high pH or with high organic matter content. Of all the micronutrients, B is the one where repeat applications are more likely as B is easily leached in coarse-textured soils, and only low rates can be applied due to the sensitivity of plants to B toxicity. Because Cu, Fe, Mn and Zn are not easily leached, it is usually economic to apply them prior to or at the time of planting rainfed crops.

Insoluble and soluble salts of Cu, Mn and Zn can work equally well in acid soils, but water-soluble fertilisers are best in alkaline or calcareous soils. The level of water-soluble Zn has been shown to be critical for optimal growth of the crop which is sown in the year that the Zn fertiliser was applied. However, it may not be important for the residual Zn effect in subsequent cropping years (Slaton *et al.*, 2005). It has been recommended that the water-soluble Zn level in Zn fertilisers be >50 % of the total Zn content of the fertiliser (Gangloff *et al.*, 2002). This has implications for the choice of Zn compounds for incorporating with macronutrient fertilisers.

Micronutrient fertilisers are routinely added to macronutrient fertilisers as carriers, and these are considered in the four categories below.

Blended fertilisers

Bulk blending of granular macronutrient and micronutrient fertilisers is widely practised. The main advantage is that a large number of blends of different volumes can be produced regionally to meet the specifications for different soils, crops and even fields. From a micronutrient point of view, the main disadvantage is that segregation can occur during blending or handling due to differences in particle size. This can result in uneven distribution of micronutrients in the field. It can be partly overcome by matching particle sizes when blending. Another disadvantage is the sparse distribution of micronutrient carriers in the blend. However, this can be overcome by dilution of the micronutrient with a suitable carrier. In a few parts of the world, dry mixes are produced in small quantities using non-granular materials. However, they are difficult to handle and caking can occur with fine particles.

Fluid fertilisers

Micronutrient compounds can be added to fluid N, NP or NPK carrier fertilisers for foliar or soil application. For example, Holloway *et al.* (2001) demonstrated the efficacy of applying Zn with fluid NP over banding $ZnSO_4$ for improved yields of wheat in a calcareous soil. Care must be taken to select the correct micronutrient sources (Silverberg *et al.*, 1972; Mortvedt, 1991). Two types of fluid fertilisers are recognized: clear liquids and suspensions (UNIDO and IFDC, 1998). Suspensions contain solid particles, either insoluble materials or soluble salts suspended in their saturated solution. Suspension micronutrient fertilisers are recommended where high rates of micronutrients are required. The micronutrient suspensions should be incorporated just before application in the field (Mortvedt, 1991). Also, such suspensions should not be left in the applicator tank overnight unless they are continuously stirred.

Compound fertilisers

In compound fertilisers (these contain two or three of the primary nutrients N, P and K), the micronutrients are incorporated during manufacture, either being added during the production of fertiliser granules or being sprayed onto the granule surfaces. In order to coat granules, most micronutrients require a binder which may be an oil, wax, water or fertiliser solution (Silverberg *et al.*, 1972). One of the advantages of coating micronutrients onto granular fertilisers is that each granule carries the micronutrient. Another advantage is that segregation of micronutrients is not a problem. The coating method can also be used for single nutrient fertilisers as well as bulk blends.

In the past, the addition of micronutrients to ordinary superphosphate during manufacture did not result in uniform content of micronutrients among granules. Chemical reactions during manufacture of compound fertilisers may decrease the availability of Zn. However, the effectiveness of Mo (Mortvedt, 1997) and B are not altered as they are unreactive. Of all the micronutrients, B is the most difficult to uniformly incorporate with NPK fertilisers. Examples of compound fertilisers with micronutrients include NPK containing 1 to 5 or 6 micronutrients, PK with B, and so on.

In many countries, there is now a wide range of high-quality compound fertilisers containing micronutrients, and these products are being produced for specific crops in designated geographical areas. To the grower, convenience, quality and consistency of product make them the fertiliser of choice. Extensive information is available in leaflets and publications from both the government and private sectors. The topic is discussed in more detail by Mortvedt (1991).

Controlled-release fertilisers

A huge range of controlled-release fertiliser (CRF) products, which contain micronutrients, is available, often targeting niche markets such as particular crops, lawn, bedding and amenity plants. These are polymer-coated (resin, plastic or wax) granules or prills designed to slowly disperse the nutrient contents into the soil (Shaviv, 2001). The nutrient-release rates vary among CRF products. Release periods specified by manufacturers are for controlled temperature conditions and, thus, actual release periods vary with field conditions. Release is much quicker at elevated temperatures, such as in soils in the tropics.

Controlled-release fertilisers are expensive to manufacture and, thus, are most suited for use in intensive horticulture, mainly glasshouses/plastic houses and containerised nurseries. They are also suitable for lawns and domestic, city and commercial gardens, where leaching of nutrients can be problematic for groundwater and surface water bodies. One of the advantages of CRFs is that they can supply micro- and macronutrients

Applications for controlled-release fertilisers:
- vegetable, fruit and cut-flower production under plastic or glass,
- containerised nursery stock,
- lawns,
- sports fields,
- urban green space,
- domestic gardens,
- indoor plants.

for extended periods from a single application. The coating reduces the potential for fertiliser toxicity and, because loss can be minimised, nutrient use efficiency may be enhanced over other forms of fertiliser.

However, on the down side, the rates of release of nutrients can be uneven (Huett and Gogel, 2000). Micronutrients may react with macronutrients to form insoluble compounds, reducing their early availability for uptake by roots.

In addition to the above controlled-release products, there are a number of other coated micronutrient formulations that have been applied to a lesser degree. These include zincated urea and resin-coated $FeSO_4$.

Foliar spray

Foliar application of micronutrients has been the method of choice for some field crops in Europe and North America as well as for many fruit, vegetable and flower crops around the world. It is increasing in importance for field crops, especially in developing countries.

Micronutrients can be foliar applied in liquid or as a suspension to crops. The decision to do so should be based on an understanding of the timing of internal demand for crop growth, the amount of nutrient that can be safely applied to the leaf, the effectiveness of foliar application and other factors. These are considered below.

Liquid foliar fertilisers can be produced by mixing salts containing the micronutrient of interest or by using commercial stabilised solutions and concentrated suspensions available on the market. Care must be taken to ensure that micronutrient fertiliser mixes are compatible with all components of tank mixes.

Micronutrients are required in small amounts and are well suited for foliar application. There are many papers in the agronomic literature that show positive yield benefits of applying foliar nutrients. However, foliar feeding should be complimentary to root feeding (Chapter 5) in most broad-acre crops, with maintenance applications being applied. Exceptions to this are soils that restrict the availability of micronutrients to the plants such as peaty soils, which strongly adsorb Cu, or calcareous soils, which limit Fe, Mn and Zn availability. In reality, corrective applications are often necessary due to the emergence of deficiency symptoms or foliar analysis data that show or predict a deficiency problem. In horticulture and other intensive cropping practices, foliar feeding may be the preferred application strategy, especially where plant nutrient status is being routinely monitored through the season and repeat spray applications can be managed. However, effects can be short-lived especially with Fe.

Foliar application is advantageous when the capacity of roots to take up nutrients cannot keep pace with the internal demand for growth. Examples include during flowering in spring when soil temperature or moisture is unfavourable for root growth, and during rapid fruit growth in some fruit trees.

The cost of foliar micronutrient application usually is low relative to the crop value (see Cost-Benefit in Chapter 5). Much smaller amounts of micronutrients are applied in foliar than in soil applications. Although repeat applications may be required on an annual basis (particularly for B, Fe and Mn), this may enable the farmer to spread the micronutrient fertiliser costs across years, particularly in developing countries, as rates used in foliar application may be 5 to 10 times lower than those applied to the soil. Over the years, some of this foliar-applied fertiliser will accumulate in the soil and provide a micronutrient bank that may be sufficient for a number of crop cycles, thus negating the need to apply foliar micronutrients each year. Furthermore, micronutrient fertilisers are often added with compatible pesticides to lower the cost of application.

Micronutrient disorders are often spatially variable within fields, and precision application of foliar sprays may be desirable depending on costs. By contrast, the unit return from applying foliar micronutrients is often greater for horticultural crops than it is for field crops. Nevertheless, foliar application may have higher economic benefits than soil application (Sarkar *et al.*, 2007; Chapter 5).

The timing of foliar application can be critical in sustaining yields or in yield recovery. This is because micronutrient demand can vary with the growth stage of the crop. Two examples illustrate this point. Firstly, in cereals, the tillering, booting and milk stages are most responsive to treatment when soil micronutrient supply is limiting. Application of Cu and B to wheat at flag leaf emergence can increase grain set by reducing pollen sterility (Chapter 3). Pollen formation is particularly sensitive to low or interrupted supply of micronutrients. Secondly, in grapevines, Zn is effective as a foliar spray for fruit set and berry development when applied two weeks pre-bloom. However, Fe may require repeat sprays due to lack of mobility, and B is necessary in the fall (autumn) to promote bud and flower initiation for the next year's crop (Christensen, 2004). Therefore, crop-specific prescriptions are necessary, and these may vary between farming districts depending on soil fertility and climate.

The ability of micronutrients taken up by leaves to move to other parts of the plant where they are needed for growth of flowers, fruits, seeds, etc. differs between elements and crop species, and sometimes between varieties. This is particularly evident for B, which may move in some plants (e.g. almond) but not in others (Chapter 5), and Fe, which is poorly mobile, as mentioned above for grapevines. Interestingly, in coffee, there is considerable B remobilization from foliar application in plants with temporary deficiency, but not in well-nourished plants (Leite *et al.*, 2007). The efficiency of use of foliar-applied micronutrients is thus partly dependent on long-distance transport inside the plant. Again, this highlights the necessity to develop and follow crop-specific prescriptions.

Leaves of crop species vary greatly in the physical (e.g. hairs, scales) and chemical (e.g. waxes, resins, cutin) barriers at the leaf surface. For this reason, other chemicals are recommended for use as co-formulants to facilitate uptake. A wide range of products is available in the market. Adjuvants are materials added to a tank mix to aid or modify the action of an agrichemical, or the physical properties of the mixture (Hazen, 2000). The most common are surfactants (surface active agents), which decrease the surface tension of the solution droplets, enabling them to spread out evenly over the leaf surface. They include ionic, non-ionic and organo-silicon formulations. Other chemicals are occasionally used to increase the retention time of the spray on the leaf (humectants) and to enhance absorption (penetrants e.g. urea). Phytotoxicity can result if the recommended fertiliser or adjuvant doses are exceeded.

Environmental conditions can strongly influence the effectiveness of a spray operation. Uptake is greater under high humidity due to the foliage retaining surface moisture for longer periods. This is particularly important in aerial application where volumes are low and microdroplets are prone to rapid drying. Spraying on overcast days or late in the day is preferred. Uptake is generally greater in young than in fully mature leaves. It may also be greater on the lower than the upper side of the leaf in some species. Leaf burning may occur under hot, sunny conditions.

The possibility to enhance the quality of food by improving the micronutrient content of cereal grain may result in another use of foliar fertilisation. For example, Duxbury *et al.* (2005) successfully fortified the Zn, Mn and Cu concentration of wheat and rice grain by this approach. However enrichment of seed late in the life cycle is not a substitute for early corrective amendments for vegetative and reproductive growth.

Turning to the elements in question, these can be considered in four categories: B, Fe, Cu/Mn/Zn, and Mo. In the case of B, there is little difference in the efficacy of the different B products available on the market as all are readily soluble. However, as the polyborates increase the pH of the solution (Peryea and Lageschulte, 2000), the final pH of the spray can vary depending on the B compound used and the buffering capacity of the water. Great care must be taken to ensure rates of foliar application do not exceed the recommended doses due to the sensitivity of plants to B toxicity. Typically, amounts of 0.1–0.5 kg B/ha are applied, and repeat foliar applications are often superior to a single dose at a higher rate.

Foliar application is the preferred method for correction of Fe chlorosis in field and many horticultural crops. Although $FeSO_4$ and Fe-chelates are widely used, reports in the literature on their effectiveness vary. Some recommend $FeSO_4$ because it is both cheap and effective (e.g. Pestana *et al.*, 2001) whereas others recommend Fe-chelates. For example, Fernandez and Ebert (2005) suggest that non-charged or negatively-charged Fe-chelates are superior to salt solutions as the Fe is more likely to be in a form that is stable and can be absorbed by the leaf. Furthermore, Fe(II) salts are readily oxidised on exposure to air and uptake can be rapid or slow resulting in toxicity or little improvement in plant condition. Other approaches to enhance Fe uptake by leaves include adding citrate to the $FeSO_4$ solution (Rombolà *et al.*, 2002), or applying Fe-lignosulphonate and Fe(III) salts at low pH, but these have limited application.

Foliar applications of Cu, Mn and Zn are very effective in correcting deficiencies. However, they are generally regarded as emergency measures where deficiencies are not recognised before sowing annual crops, but may be routinely practised for many horticultural and perennial crops, and field crops grown on soils where nutrient availability is problematic. The most common inorganic compounds used are: Cu-oxychloride, Mn-sulphate and Zn-sulphate at the rates of 0.5-4 kg Cu/ha, 1-5 kg Mn/ha and 1-2 kg Zn/ha. Generally, the chelates are effective (e.g. Rosolem and Sacramento, 2001) and lower rates can be used so helping to offset the higher costs of the ingredients. However, Papadakis *et al.* (2005) showed that $MnSO_4$ was more effective than Mn-EDTA in improving the Mn status of citrus. Other organic complexes, such as the lignosulphonates, have also been shown to be effective but are not widely used. Note that $CuSO_4$ can cause phytotoxicity and, thus, is rarely used unless mixed with lime.

Another benefit of applying these metals to foliage is that they have a fungicidal effect on the leaf surface and can help to reduce infection of some pathogenic fungi.

To overcome Mo deficiency in acid and sandy soils, Mo can be applied as a foliar spray using $Na_2MoO_4.2H_2O$ or $(NH_4)_6Mo_7O_{24}.4H_2O$ at the rate of 50-150 g Mo/ha. Responsive crops include grain and pasture legumes (biological N_2 fixation requires Mo), members of the cabbage family, sugar beet, tomato and tobacco, amongst others. Molybdenum is readily translocated from leaves to root nodules so this is an effective means of applying Mo for legumes. Application of foliar Mo can also improve the yield and berry quality of grapevines (Williams *et al.*, 2004).

Fertigation

When water-soluble fertilisers are delivered to crops in the irrigation water, this is known as fertigation. Trickle or drip irrigation systems are widely used for fruit trees, roses and containerised nursery stock. However, microspray or sprinkler systems may also be used.

Fertigation effectiveness is dependent on having operational fertiliser management programs where fertiliser scheduling matches the crop requirement at different stages

Advantages of fertigation:
- precision application of nutrients (Bar-Yosef, 1999);
- able to adapt fertiliser supply to crop demand;
- control over the concentration and composition of nutrients in the root zone;
- greater crop uniformity;
- improved nutrient use efficiency compared to soil application of solid fertilisers;
- supplies nutrients to roots in forms available for uptake (e.g. Fe to roots in calcareous soils where Fe deficiency is problematic or Cu to roots in nursery mixes high in organic matter content that strongly sorb Cu);
- nutrient disorders can be rapidly corrected;
- composition and/or rate of nutrients can be altered based on leaf analysis;
- nutrient application is often not weather dependent;
- reduced fertiliser wastage unless provided by overhead sprinklers;
- leaching of nutrients is minimised;
- able to regulate vegetative growth in favour of fruit quality such as in grapevines.

Disadvantages of fertigation:
- high capital cost of equipment, including irrigation lines, pumps, filters and fertiliser injectors;
- regular monitoring is required;
- high cost of maintenance;
- need for irrigation water to be of good quality (pH, salinity, hardness, Fe content, etc.). Water with too much Fe or Ca can be especially problematic due to precipitation in inline and other outlets.

of its life cycle across seasons. The micronutrient fertilisers must be soluble and remain in solution. To avoid chemical reaction with some of the macronutrient fertilisers, micronutrients can be applied separately through the irrigation system. Though more expensive than inorganic salts, chelated forms of Cu, Fe, Mn and Zn are recommended in order to maintain solubility, minimise precipitation and to achieve more even distribution. Any of the commercial B fertilisers is suitable for fertigation. The use of compound fertilisers containing micronutrients is to be avoided as the quality of the dissolved material varies due to variation in solubility and composition.

Hydroponics

Soil-less systems are widely used for the production of greenhouse crops such as lettuce, tomato, strawberry, cutflowers and ornamental plants. Increasingly, clonal banks are grown hydroponically in forest nurseries because of superior cutting performance. Plants can be grown in an inert material such as gravel, sand, perlite and rockwool moistened with nutrient solution, or the root system can be bathed by the nutrient solution as long as it is well aerated. In aeroponics, the nutrient solution is pulsed as a spray onto the roots. From a nutrition point of view, advantages of this production system are the high efficiency of nutrient (and water) use, and the opportunity to change the composition of the nutrient mix depending on the requirements for the growth stage of the crop. Other advantages include the capacity to grow produce under adverse conditions and without arable soils, reduced pollution and enhanced efficiency that comes with intensive production. In hot climates, aeroponics has an advantage over nutrient film technique in reducing root-zone temperatures.

Unlike in soil, hydroponic systems are not buffered, either for pH or nutrient supply to the root system. So, nutrient concentrations are considerably higher than in soil solution. However, micronutrient concentrations can be 2-10 times lower with flowing solution culture (Wild *et al.*, 1987; Parker and Norvell, 1999) or nutrient film techniques, because the nutrients can be recycled and replenished. Typical concentrations of micronutrients used are (μM): B 20, Cu 0.8, Fe 30, Mo 0.5, Mn 10 and Zn 3.

Hydroponic crops require intensive management, but once crop-specific recipes are optimal, the production system can be automated. As for fertigation, the micronutrient fertilisers must be water-soluble and remain in solution. The option for separating the supply of macro- and micronutrients temporally does not apply, so extra care must be taken in selecting compatible compounds. Whilst proprietary micronutrient products are available, growers can also make their own blends from single micronutrient compounds.

Ferrous sulphate is not recommended as an Fe source as it is quickly oxidised and then precipitates as $Fe(OH)_3$. Iron chelates are generally preferred, and a range of chelates are available, differing in their stability to pH. One of the problems with Fe chelates is that their colour decreases the UV transmittance required to disinfect the nutrient solution. Also, UV and ozone disinfection can decompose the chelating agents, resulting in precipitation of Fe as $Fe_3(PO_4)_2.8H_2O$ (Demeyer *et al.*, 2001).

Seed treatment

Seed treatment is the most common method to apply Mo to legume crops. Seeds can be primed by either coating the seed with some kind of sticking agent as a slurry/liquid, or by soaking the seed in a dilute Mo solution. One advantage of this method is that each plant receives a dose of Mo. Another is that farmers can easily treat the seed. Johansen *et al.* (2005) found that chickpea yields were increased by 22 % when seed was soaked for 8 hours in a solution containing 0.5 g $Na_2MoO_4.2H_2O$/l.

Usually, the seed is inoculated at the same time with a compatible *Rhizobium* strain; so care must be taken to ensure the bacteria are not adversely affected. Gault and Brockwell (1980) showed that lucerne and clover *Rhizobium* were adversely affected by $Na_2MoO_4.2H_2O$, but not by $(NH_4)_6Mo_7O_{24}.4H_2O$. Molybdenum trioxide is an alternative if there is a salt effect, and it can be mixed with lime as it is insoluble.

Seed coating with other micronutrients (B, Fe, Mn and Zn) has also been tried but is not widely practised. The addition of Fe to seeds is usually only sufficient to provide for growth of a few leaves in calcareous soils.

Other methods

Alternative strategies to deliver micronutrients to plants on a limited scale involve dipping roots into a micronutrient solution and the injection of liquid or solid fertiliser into the trunks of trees. To prevent Zn deficiency in rice, roots of seedlings can be dipped in a 2-4 % ZnO suspension before transplanting or the seeds can be pre-soaked in the same solution (Dobermann and Fairhurst, 2000). Trunk injection is suitable for reversing symptoms of micronutrient disorders in fruit and urban trees. So far, deficiencies of Cu, Fe, Mn and Zn have been corrected this way. The process is expensive and only has commercial applications for high-value trees.

Additional reading

Alloway, B.J. (2008). *Zinc in Soils and Crop Nutrition*, 2nd ed. IZA and IFA, Brussels and Paris.

Andersen, P., Tuladhar, J.K., Karki, K.B. and Maskey, S.L. (2005). *Micronutrients in South and South East Asia*. International Centre for Integrated Mountain Development, Kathmandu.

Bar-Yosef, B. (1999). Advances in fertigation. Advances in Agronomy 65: 1-77.

California Plant Health Association (2002). *Western Fertilizer Handbook*. Interstate Publishers, Danville.

Fageria, N.K. (2008). *The Use of Nutrients in Crop Plants*. CRC Press, Boca Raton.

7. Best Management Practices (BMPs) for micronutrients

Micronutrients should be considered within broader Integrated Plant Nutrition Systems (IPNS), which aim to "enhance soil productivity through a balanced use of local and external sources of plant nutrients in a way that maintains or improves soil fertility and is environmentally-friendly" (FAO, 1995). More recently, Welch and colleagues (Welch and Graham, 2005) argue that even IPNS are not sufficiently broad as a nutrient management framework and that best management practices for micronutrients should also consider nutrients in the food chain.

Integrated Plant Nutrition Systems

IPNS are used to maintain or adjust soil fertility and plant nutrient supply to achieve a given level of crop production. This is done by optimizing the benefits from all possible sources of plant nutrients (FAO, 1995).

The main objectives are to:

- maintain or enhance soil productivity through a balanced use of mineral fertilisers combined with organic and biological sources of plant nutrients;
- improve the stock of plant nutrients in the soil;
- improve the efficiency of plant nutrients, thus limiting losses to the environment.

In the context of IPNS, best practices are built on the use of micronutrients in agriculture, horticulture and forestry to maximize the benefits and minimize the possible negative effects associated with their application. In principle, micronutrients supplied in optimal forms and amounts and with optimal timing and placement, on soils with an inadequate supply, will generate benefits for producers, providing other factors are not limiting.

In the preceding chapters, the principles governing optimal supply, methods of application and timing of application have been discussed. These principles and practices are key ingredients in fertiliser BMPs (Stewart, 2006). The best management principles for micronutrients are summarised below. Provided these principles are adopted and there is a sound knowledge of inputs and outputs of micronutrients in the farming system, negative effects of micronutrients should be negligible or manageable. By considering the implications of micronutrients in harvested plant products for human nutrition, the benefits can be further extended.

Principles for BMPs for micronutrients in agriculture, horticulture, and forestry:

- identify other limiting factors and correct them before or while applying micronutrients;
- select optimal rate, fertiliser type, method of application and time of application for effective correction of deficiency;
- determine residual effects of the micronutrient application over time, including possible toxicity effects on following crops;
- calculate nutrient budgets to identify all sources of micronutrient input and output to detect declining supply or the accumulation of excess;
- monitor levels in crops and soils by soil and plant analysis;
- utilise genotypic efficiency;
- manage crop nutrition to achieve adequate micronutrient levels in harvested products for human nutrition.

Alleviation of other limiting factors

On soils low in micronutrients, there may be limited or no benefit from applying them to the soil as fertiliser if other major constraints are limiting production. For example, acute NPK deficiencies may mask the consequences of low soil micronutrient levels. Bell *et al.* (1990b) reported that, across 15 B-responsive sites in Thailand, there was only a weak yield increase to B fertiliser alone (Fig. 7.1). At the same sites, with basal fertiliser applied rates in kg/ha of 25 P, 30 K, 23-116 S, 116 Ca and 0.53 Mo, B response was much greater.

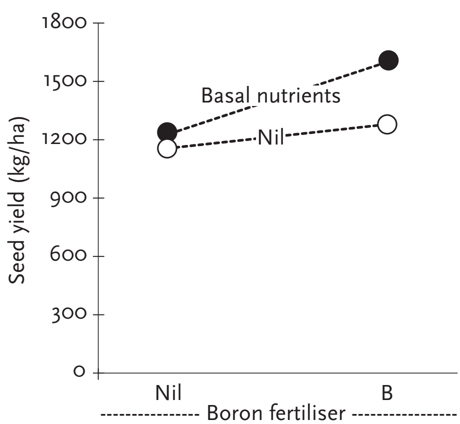


Figure 7.1. Effects of boron fertiliser on peanut seed yields (kg/ha) with and without basal nutrients applied (Bell *et al.*, 1990b). Values are means from 15 sites with acid sandy soils in north-east Thailand (Average properties across 15 soils: % clay, 11 % silt, 81 % sand, pH (1:1) H_2O 5.1; hot water soluble B 0.1 mg/kg).

Constraints such as soil acidity, low soil water, pests and diseases, if not treated, may limit crop production to an extent that the use of micronutrients fails to increase crop yields and hence may be uneconomic, unless there was a tangible benefit from improved product quality or nutritional quality.

Residual effectiveness of added micronutrients

The amounts of micronutrients needed for a particular crop are generally small compared to the amounts of macronutrients applied. The amounts of micronutrients required are also small compared to the amounts of micronutrients recovered in the first crop. Hence, in general, low rates of micronutrients are sufficient for optimum crop production (see Chapter 5). These amounts may remain effective in the soil for many years of crop production. For example, Brennan (2005) calculated that a single Zn application of 0.75 kg Zn/ha, when applied to low-Zn soils in south-west Australia, would support as few as six and up to an infinite number of wheat crops depending on grain yield, Zn sorption capacity of the soils, and the presence or absence of Zn impurities in P fertilisers.

Brennan (2005) then calculated for typical rotations, the length of time that a single Zn application would likely maintain an adequate Zn supply (Table 7.1). This scenario assumes an initial application of 0.75 kg Zn/ha, plus 0.09 kg Zn/ha once every rotation cycle as an additive in the superphosphate applied to the pasture in the rotation. At yield levels that are relatively high for south-west Australia, Brennan (2005) calculated that a repeat Zn application was not needed until after 18 years (Table 7.1). Calculations assume the application of Zn as an additive in superphosphate supplied to the pasture, but negligible amounts of Zn supplied in ammonium phosphate fertiliser applied to the crops. Based on soil Zn sorption studies, 70 % of the applied fertiliser Zn was assumed to remain in the plant-available pool after application. Field experiments in south-west Australia have been running for over 20 years without evidence of Zn deficiency re-emerging after the initial application of Zn fertiliser (R. Brennan, personal communication). At a moderate yield level, the residual fertiliser Zn plus annual Zn supplements in superphosphate would maintain an adequate supply for an estimated 150 years or more.

Table 7.1. Budget for Zn inputs and outputs for a typical rotation followed in south-west Australia on a low-Zn sandy loam soil with an initial application of 0.75 kg Zn/ha, as recommended (Brennan, 2005).

	Yield (t/ha)	Zn in produce (mg/kg)	Zn removed (g/ha)	Zn added (g/ha)	Zn balance (g/ha)
Pasture and clean wool	0.04	110	3.5	90	86.5
Wheat	1.5	22	33	0	-33
Lupin	1.1	30	33	0	-33
Canola	1.1	30	33	0	-33
				Sum	-12.5

Similarly, for Cu fertiliser supply in the farming system of south-west Australia, Brennan (2005) reported long residual effectiveness of a single Cu application. At the recommended rate of initial application (1.38 kg Cu/ha), the first evidence of Cu deficiency re-appearing occurred after 28 years. At half the recommended Cu rate, Cu deficiency re-appeared in wheat after 16 years. The long residual value of the Cu fertiliser was attributed to the fact that a wheat crop was sown every 4 years, with pastures in the intervening years, and to the fact that each wheat crop only recovered 2-3 % of the initial Cu application.

The south-west Australian examples are based on a low-output dryland agricultural system with average annual grain yields in the range 1.5-3 t/ha, and they do not represent the residual effectiveness of micronutrients under all conditions.

For an intensive irrigated rice-wheat rotation, which is common in south Asia (Ladha *et al.*, 2003), with total grain yields of 10-12 t/ha/yr, an initial Zn fertiliser application of 0.75 kg Zn/ha would only remain effective for 1-2 years, depending on the Zn sorption capacity of the soil (Fig. 7.2). Indeed, annual Zn applications have been practised in the more intensively managed areas of rice-wheat cultivation, and on alkaline soils with considerable Zn sorption capacity. Such applications have decreased the incidence of

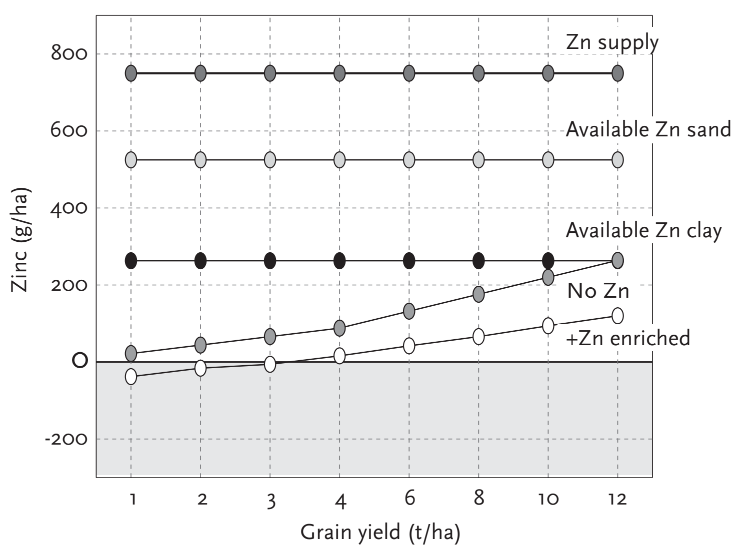


Figure 7.2. Simple model to estimate Zn residual effectiveness based on the relationship between Zn supply, soil Zn sorption and crop yield. The figure plots cumulative Zn uptake as a function of grain yield in scenarios where no Zn is added or where Zn-enriched macronutrient fertilisers are applied. The Zn supply refers to an initial fertiliser Zn application of 0.75 kg Zn/ha. Available Zn levels refer to the proportion of the applied fertiliser Zn that remains in the plant available pool, and depends on the Zn sorption capacity of the soil which, in the model, varies from 30 to 70 % based on Brennan (2005).

Zn deficiency. While soil Zn levels need to be monitored in this system to avoid the accumulation of excessive soil Zn, simple mass balance calculations for Zn suggest that most of an annual application of 0.75 kg/ha would be removed in the harvested grain (Nayyar *et al.*, 2001). Therefore, in the intensive rice-wheat system of the Indo-Gangetic Plain, Zn fertiliser rates are typically 5-11 kg Zn/ha (Nayyar *et al.*, 2001).

Yield is clearly a major determinant of the residual value of added micronutrient fertilisers. Accurate prediction of yield improves the prospects of correctly estimating when further application of micronutrient fertilisers is necessary to maintain adequate supply. Accurate records of yields in a field since last application of micronutrients will ensure that appropriate decisions are made about the time for re-supply of micronutrients. Regardless of the intensity of the cropping system, substantial removal of straw from fields would further decrease the length of residual micronutrient effects on crop production.

Boron has different behaviour in soils compared to that of Zn and Cu because it is more prone to leaching and the risk of toxicity is greater (Shorrocks, 1997). Boron-cycling studies in the oilseed rape-rice-rice cropping system were conducted on three key soils in south-east China (Wang *et al.*, 1997; Wei *et al.*, 1998; Wang *et al.*, 1999; Yang *et al.*, 2000). Results showed that, even with repeated annual applications of 3.3 kg B/ha/yr to the oilseed rape for three consecutive years, no evidence of B toxicity was found. This was consistent with the extractable-B levels that only increased modestly in the 0-20 cm layer.

Part of the reason for the small increase in extractable B in the 0-20 cm layer was that B was redistributed to greater depths in the soil. However, no leaching loss of B was measurable below 80 cm depth, even on a sandy alluvial soil. Over 40 % of the B added initially was removed over a 3-year period in harvested grain and straw. Hence, in this intensive triple cropping system in south-east China, it was concluded that B toxicity risk was low. Little B was lost by leaching, but removal of B in harvested crops and crop straw was the major cause for the decline in residual B over time. It was estimated that 1.65 kg B/ha should be re-applied every three years in this cropping system (Yang *et al.*, 2000).

On sandy loams derived from sandstone in the uplands of south-west China, repeat applications of B are required to meet the replacement requirements for eucalyptus plantations following harvest (Dell *et al.*, 2003). Over the full length of the rotation, the plantation has a large requirement for B. Boron was sequestered mostly in the wood, and unable to be redistributed to the new shoots as they develop, and the soil has limited capacity to retain B added as fertiliser. In this system, supplying the whole B requirement of the rotation at planting and then relying on residual effectiveness is not satisfactory, since the required rates cause B toxicity in the first year. Lower rates, which avoid B toxicity, only last for 2-4 years, after which B deficiency re-appears.

For Mo, the main factor governing residual value appears to be Mo sorption by the soil, although crop yields, and species and cultivar differences in Mo uptake are also important. On soils with limited Mo sorption, residual Mo from a small initial application of 0.11 kg/ha was sufficient to prevent the return of Mo deficiency for 15 years (Riley, 1987). By contrast on acid Oxisol soils in southern Queensland, Australia, residual Mo corrected Mo deficiency for only 2-5 years, depending on plant species (Johansen *et al.*, 1997). The soils with the highest initial Mo rate required to correct deficiency also had the shortest residual effect of the added Mo due to their high Mo sorption capacity.

In more extreme cases of strong Mo sorption by soils, application of Mo at 0.14 kg/ha only corrected Mo deficiency in the year of application (Riley, 1987). Some crops continue to respond to annual Mo application even after 20 years of annual Mo applications on acid soils of eastern Australia (Smith and Leeper, 1969). For cauliflower, which has a high Mo requirement, an application of 1.8 kg Mo/ha was necessary to achieve continued correction of Mo deficiency for three years (Mortvedt, 1997). Such rates are an order of magnitude higher than those used in most crop and pasture species that have a lower Mo demand.

The decline in residual value of Mn and Fe fertiliser on alkaline soils is even more extreme than the case of Mo. It is recognised that the residual value of Mn fertiliser for succeeding field crops on alkaline soils is negligible or very limited (Reuter *et al.*, 1988). Indeed, the rapidity and extent of Mn reversion to low solubility manganic forms may require repeat Mn fertiliser supply as soil or foliar applications, even in the same year of application, to prevent the return of deficiency (Graham *et al.*, 1985). The reversion of soluble Mn is attributed to the formation of well-ordered Mn forms that are difficult for roots to extract. By contrast with its poor residual effectiveness on alkaline and neutral soils, the residual effects of Mn fertilisers on acid sandy soils can be substantial.

Soil application of Fe salts on alkaline soils is considered to be worthless under most circumstances, since the rapid oxidation of Fe(II) to Fe(III) renders salts of Fe completely ineffective as fertiliser in a very short period of time. Iron chelates are used to deliver Fe to high-value crops as they do remain effective for the whole growing season on alkaline soils, but their high price limits regular use in field crops or by low-income farmers. Moreover, Fe chelates have low residual effectiveness in subsequent crops; so repeated annual applications are needed to control Fe deficiency on alkaline soils.

Given that much of the micronutrients applied in fertiliser are not used in the first crop, their residual value and fate in the soil are key factors in predicting and managing possible negative consequences on the environment and for human health. An understanding of the extent of soil reactions with the added micronutrients, and of the micronutrient inputs and outputs in the cropping system (i.e. the nutrient budget) is essential for managing micronutrient supply.

Nutrient budgets

As shown above, in individual fields, nutrient budgets can be a useful way to monitor the balance between inputs and outputs of micronutrients. Relatively simple spreadsheet calculations of the type shown in Table 7.1 and Fig. 7.2 could be adopted as part of best practice on farms to identify and quantify all sources of micronutrient inputs and outputs. The input-output calculation serves two purposes: firstly, to identify deficiencies likely to appear over time and, secondly, to identify risk of significant accumulation of micronutrients over time. Table 7.2 lists probable inputs and outputs that need to be quantified in calculations of micronutrient budgets.

Table 7.2. Key micronutrients inputs and outputs that need to be quantified in order to calculate a nutrient budget.

Inputs	Outputs
Fertiliser	Grain, fruit, leaves, wood or other harvested products
Impurities in macronutrient fertiliser, soil amendments	Straw
Organic nutrient sources (Animal manure, biosolids, etc)	Plant litter
Fungicides and pesticides	Eroded sediments
Seed or plant propagules	Leaching
Irrigation water	
Rainfall and atmospheric accretion	

Many materials applied on farms contain micronutrients. These materials may contribute significantly to the micronutrient budget and, if their continued use is not accounted for, eventually, they could become the source of negative environmental impacts. Commonly, macronutrient fertilisers are enriched in micronutrients as a low-risk strategy to supply a deficient element. In south-west Australia, 500-600 mg Zn/kg of fertiliser has been added in superphosphate for over 30 years, and it is sufficient to replace Zn removed in harvested products. Boronated fertilisers are commonly used to provide B as an additive in NPK formulations or superphosphate, with a B concentration generally of 200-600 mg B/kg (Bell *et al.*, 1990b).

Enrichment of macronutrient fertilisers with micronutrients is designed to supply the needs of the immediate crop, but provides limited residual inputs to the soil. This minimises the risk of accumulation over time and hence minimizes the risk of toxicity. All macronutrient fertilisers contain background levels of micronutrients, even when not purposely added. At fertiliser rates that supply 120 kg N, 26 kg P and 48 kg K/ha, Nayyar *et al.* (2001) reported that significant amounts of Zn, Mn, Mo and B were added to soils (Table 7.3). Such quantities of micronutrients may be significant in the nutrient budget and need to be accounted for. Batches of fertiliser with the same formulation may vary in background micronutrient content. This also needs to be considered in constructing the micronutrient budget. Moreover, from previous studies (Bell *et al.*, 1990b; Nayyar *et al.*, 2001), single and triple superphosphate appear to contain higher levels of B, Cu, Mn, Mo and Zn compared to urea, muriate of potash and ammonium sulphate.

Table 7.3. Estimates for addition of micronutrients (g/ha) to soils by different combinations of fertilisers designed to supply 120 kg N, 26 kg P and 48 kg K/ha (Nayyar *et al.*, 2001).

Fertiliser combinations	B	Cu	Mn	Mo	Zn
Ammonium sulphate, superphosphate, KCl	51	7	336	132	70
Urea, triple super phosphate, KCl	29	7	10	38	53
Urea, diammonium phosphate, KCl	54	1	41	14	17

Apart from the planned application of micronutrients in fertilisers supplied to crops, micronutrients may enter the farming system from other sources such as biosolids, animal manures, and from crop protection products. Other soil amendments like gypsum or fly ash may contain high levels of micronutrients. In Thailand, for example, gypsum contained up to 4700 mg Zn/kg (Bell *et al.*, 1990b). Since soil amendments like lime and gypsum are added in relatively large amounts, they are potentially a significant source of micronutrients even when the concentration in the material is not large (Zarcinas and Nable, 1992). Copper fungicide used over a long period has caused considerable contamination of soils in citrus orchards in Florida (Alva, 1993), vineyards in France (Delas, 1963), and in other fruit and vegetable crops (Tiller and Merry, 1981).

Accretion of B in rainfall may be a significant input in the B budget, depending on total annual rainfall and proximity to the sea (Bell, 1999). Similarly, accretion of micronutrients from atmospheric deposition may be significant in the vicinity of industrial and minerals processing plants.

Soil and plant analysis

In addition to nutrient budgets, an accepted means of verifying micronutrient levels in soils and crops is the use of soil and plant analysis (Mortvedt *et al.*, 1991; Reuter and Robinson, 1997; Peverill *et al.*, 1999). Soil analysis is used to predict the likely occurrence of micronutrient deficiencies and to monitor changes in soil status over time (McLaughlin *et al.*, 1999).

When used for prediction of a likely deficiency, a soil sample taken before sowing can be analysed to determine what corrective fertiliser application is needed to avoid the deficiency. This use of soil analysis is most helpful to growers since it allows for a corrective action before yield loss is experienced. Monitoring the levels of soil micronutrients over a period of time allows land managers to detect trends in status and to adjust fertiliser programmes accordingly, to avoid either deficiency developing or excess accumulating in the soil.

Plant analysis can be used for the same outcomes in crop nutrition but, in addition, it is useful for diagnosing deficiencies in a standing crop (Smith and Loneragan, 1997). Hence, where a deficiency occurs unexpectedly during the growing season, analysis of selected leaves or plant parts offers the possibility of diagnosis of the disorder. If completed in a timely fashion, plant analysis provides information for the grower to decide on corrective action for the current crop.

Micronutrient analysis of soils and plants can only produce reliable results if extreme care is taken to avoid contamination of the sample. The care required greatly exceeds that required with collecting and handling samples for macronutrient analysis. Minute amounts of a contaminant are sufficient to cause erroneous results with micronutrient analysis.

Implements used to collect, store or handle samples need to avoid materials that contain micronutrients (see box below). Even Cu studs on articles of clothing worn by the sample collector or analyst have been known to cause erroneous soil and plant analysis results due to sample Cu contamination.

To prevent micronutrient contamination of samples for soil or plant anlaysis, implements used to collect, store or handle samples need to avoid materials that contain:

- galvanised iron (source of Zn),
- copper or brass fittings (sources of Cu),
- rubber (source of Zn),
- white pigmented plastics (sources of Zn),
- certain fungicides (sources of Cu, Mn or Zn),
- certain insecticides (sources of B),
- borosilicate glassware (source of B), etc.

The basis for interpretation of soil analysis results is a set of concentration ranges calibrated to determine whether levels of the nutrient extracted from the soil are insufficient, adequate or excessive for crop growth, yield or quality. Calibration of a soil test is usually achieved by relating the soil extractable nutrient levels at several sites to the respective crop yields. This involves establishing a sampling protocol that specifies the soil analysis method, the soil sampling depth and time. An example of such a calibration relationship is shown in Fig.7.3 for the relationship between extractable B and oilseed rape seed yields (Wei *et al.*, 2002). In this case, the extractable soil B in the 20-40 cm soil layer was better correlated with seed yield of oilseed rape, and it gave a narrower critical range of 0.4-0.52 mg B/kg compared to 0.5-0.66 mg B/kg in the 0-20 cm layer. However, when a calibration of a soil test has been developed, a number of factors affect the accuracy of predictions. These are listed in the box below.

Calibration of soil tests and, hence, the accuracy of predictions using a soil test depend on:

- the type of extractant used,
- the depth of soil sampling,
- the soil type,
- growing season conditions,
- crop species,
- whether the assessment is for optimal yield or crop quality.

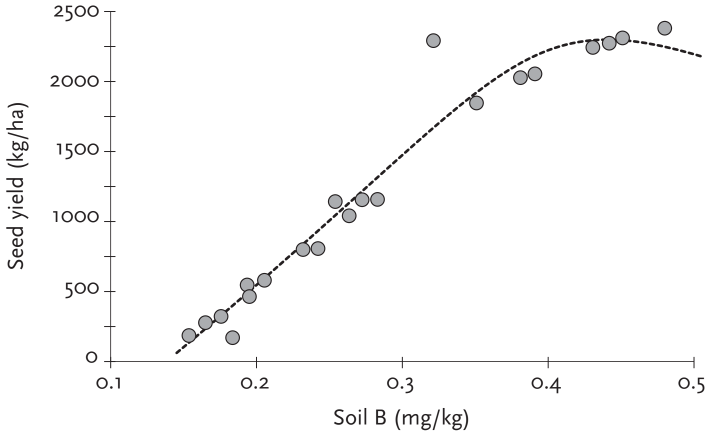


Figure 7.3. Relationship between hot CaCl2-extractable soil B in the 20-40 cm depth and seed yield of oilseed rape in 10 field experiments using the polynomial regression model. $Y = -275 + 4696x + 59304x^2 - 80227x^3$. $R^2 = 0.971$ (Wei *et al.*, 2002).

Generally, good relationships are obtained between yield and soil-extractable Zn or B when considering a limited range of soils (e.g. Bell, 1999). However, when the range of soils broadens, separate relationships may be needed for related classes of soils or, alternatively, multivariate relationships are often able to improve the relationship (McLaughlin *et al.*, 1999). In a similar vein, Martens and Lindsay (1990) suggested that the DTPA extraction, which was developed for predicting Fe, Zn, Mn and Cu deficiency on alkaline and calcareous soils, may require inclusion of soil pH in models to predict micronutrient cation deficiencies in a broader range of soils (e.g. Brennan *et al.*, 1992a; b).

Among the micronutrients, soil testing has possibly been most effective for predicting B deficiency (Bell, 1997). Soil B testing has been used for several decades but, even today, most methods are based on the method of Berger and Truog (1939), which extracted B by hot water. Modern variations use hot 0.01 M $CaCl_2$ extraction to improve the flocculation of soil extracts. While successful prediction of B deficiency is reported for many crops and soils (Moraghan and Mascagni, 1991), soil analysis has not been reliable in detecting soils that produce B deficiency in crops in other instances (Sims and Johnson, 1991). However, as with other micronutrients, it is likely that critical values for predicting deficiency of B will vary with soil texture and soil pH (Table 7.4).

Critical B values will also vary with depth of soil (see Fig. 7.3) but, curiously, few of the reports in Table 7.4 specify a soil depth in the sampling protocol. Critical B values reported for wheat and black gram on alkaline soils are 2-4 fold higher than on neutral-acid soils (Bell, 1997). In addition, environmental factors such as soil water content may also affect the critical values required to avoid B deficiency. Finally, as with all micronutrients, critical values vary among species depending on their sensitivity to B deficiency, and among cultivars of a species that vary in B efficiency (Table 7.4).

Table 7.4. Critical boron concentrations (mg B/kg soil) or concentration ranges in field soils for the prognosis of B deficiency.

Species	Method of extraction: soil sampling depth (cm)	Soil pH	Critical B concentration or concentration range	Country; source
Bean	HWS[1]: not reported	7.6	0.4-0.5[2]	Colombia; Howeler *et al.* (1978)
Black gram	HWS: pot experiment	7.7-10	0.53	India; Sakal *et al.* (1985)
Black gram	HWS: 0-25 cm	5.5-6.5	0.08-0.13	Thailand; Bell *et al.* (1990b)
Broccoli, Brussel sprouts, Cauliflower[3]	HWS: not reported	5.8-6	0.28-0.34	Canada; Gupta and Cutcliffe (1973; 1975)
Peanut[4]	HWS: not reported	5.0-7.7	0.15	USA; Morrill *et al.* (1977)
Peanut[5]	HWS: 0-10 cm	na[6]	0.14-0.16	Thailand; Bell *et al.* (1990b)
Rutabaga[7]	HWS: not reported	5.2-5.4	0.65-0.9	Canada; Gupta and Cutcliffe (1972)
Wheat	HWS: not reported	na[6]	0.12-0.15	Thailand; Rerkasem *et al.* (1988; 1989)
Wheat	HWS: not reported	alkaline	0.32-0.38	China; Li *et al.* (1978)

[1] HWS - hot water soluble.
[2] Howeler *et al.* (1978) reported a critical value of 0.65 mg B/kg soil, but examination of their data suggests a lower critical range.
[3] Critical range obtained by combining the lowest B concentrations from Gupta and Cutcliffe (1973) where leaf B was adequate for yield and symptoms were absent, with the highest values of Gupta and Cutcliffe (1975) where yield was depressed or symptoms were present.
[4] Critical values for the elimination of hollow heart disorder in kernels.
[5] Critical values for < 5 % hollow heart incidence in kernels.
[6] pH of soils in the study not reported.
[7] Critical values for brown heart disorder in roots at maturity.

A selection of critical Zn values in soils is shown in Table 7.5. However, Brennan and colleagues (Brennan and Gartrell, 1990; Brennan, 1992a; b) found that the critical soil Zn values across a wide diversity of Australian soils were best explained by a multivariate regression that included soil pH and $CaCO_3$ as well as DTPA-extractable soil Zn. Therefore, the critical ranges should be used with caution when applied across a wider range of soil types than used in the original calibration of the test.

Table 7.5. Critical ranges of DTPA-extractable soil Zn for various crops in field trials in Australia (Brennan, 1999b).

Species	Soil sampling depth (cm)	Soil texture	Critical Zn concentration (mg/kg)
Barley	0-10	Sandy loam, sands	0.41
Field pea	0-10	Various	0.48
Wheat	0-10	Various	0.8

Soil analysis has had mixed success for predicting Fe, Mn, Cu and Mo deficiencies. Martens and Lindsay (1990) concluded that soil analysis is a useful approach for crop management. This is despite the degree of uncertainty that often exists between deficient and adequate soil test values for micronutrients. By contrast, Reisenauer (1988) and Uren (1999) expressed doubts about the feasibility of developing accurate soil tests for prediction of Mn deficiency. The different forms of Mn in soils respond to redox reactions, and their dynamic change over time means that a soil extractant, removing Mn at a single point in time from arbitrary pools of soil Mn, is unlikely to predict the amounts of plant-available Mn in soil for a crop over its growing season. This is especially evident as many species modify Mn availability in the rhizosphere by excretion of chelates and reductants. Martens and Lindsay (1990) indicate that Mn deficiency is very weather-dependent, and that it affects the accuracy of Mn soil tests.

According to Brennan and Best (1999), soil tests for Cu are most reliable when restricted to soils with similar properties. Prediction of Cu deficiency by soil analysis is improved by taking into account other soil properties such as pH, CEC, organic matter, hydrous oxides and silt plus clay content. Jarvis (1981) suggested that plant factors also need to be considered in using Cu soil tests for prediction of deficiency.

Many soil, plant and environmental factors affect the interpretation of soil Fe test results but, generally, soil tests are ineffective in predicting the plant-available forms of soil Fe (McFarlane, 1999). According to McFarlane (1999), soil pH, moisture and bicarbonate concentration, and genotypic variation affect Fe uptake to such an extent that soil Fe tests are very difficult to calibrate. In addition, soil tests on bulk soil are not likely to predict what is available for plant uptake because plants have an extraordinary capacity to modify the forms and availability of Fe in the rhizosphere (Marschner, 1995).

Apart from predicting the possible deficiency of micronutrients for crop production, soil tests may be useful in predicting soil levels of micronutrients that are toxic to plants and potentially harmful to the environment (Alloway, 1995).

Plant analysis has a complementary role to that of soil analysis for the management of micronutrient deficiencies. Like soil analysis, plant analysis can be used for the prognosis of deficiency. Their main objective is to predict the likelihood of a deficiency emerging at some future time in the crop growth cycle to limit production (Smith and Loneragan, 1997). When used in this modality, plant analysis has a disadvantage relative to soil analysis in that the crop is already growing. Hence, there may be insufficient time available after acquiring the plant analysis results to apply a corrective treatment, especially with short-duration annual crops.

Plant analysis results are direct measures of the status of plant nutrients, and they integrate the influence of many soil factors that affect micronutrient availability. Nevertheless, plant analysis needs to be calibrated against crop response before it can be used effectively for prediction of the likely response to fertiliser.

An example of a calibrated relationship between leaf B and seed yield is shown in Fig. 7.4. For oilseed rape, the youngest open leaf (YOL) was selected as the sampling part because its B concentration was strongly responsive to increasing B supply and well

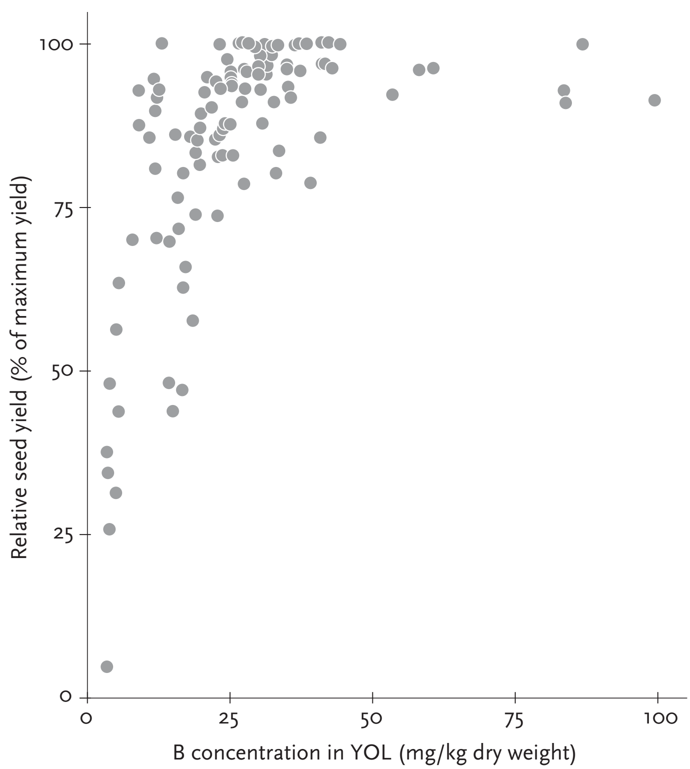


Figure 7.4. Relationship between B concentration (mg/kg) of the youngest open leaf (YOL) at the seedling stage (Growth stage 1,8-1,10 after Sylvester-Bradley, 1985) and relative seed yield in 10 field experiments conducted with oilseed rape in Zhejiang Province, China, in 1992-1993. Maximum seed yield was designated as 100 % and all other yields in that replicate block were calculated as a percentage of the maximum (Wei *et al.*, 1998).

correlated with seed yield response. Youngest open leaf samples were collected about 6-8 weeks after transplanting when the plants were at a vegetative growth stage with 8-10 leaves (Sylvester-Bradley, 1985). In this study, the best model of the relationship between YOL-B concentration and yield was the Mitscherlich equation, which explained 68-89 % of the variation in the data. The calculated critical range in the YOL at seedling stage was 20-25 mg B/kg, and it appeared to be valid across two seasons and three soil types. The critical B range for prognosis of B deficiency was found to consistently predict low soil B and those crops in farmers' fields that had low seed yield (Wei *et al.*, 1998).

Other calibrated critical ranges for predicting B deficiency by plant analysis are shown in Table 7.6. These values illustrate how the critical range typically declines with plant age, emphasising the importance of standardisation of sampling time in order to make meaningful interpretation of the results. Among plant species, there is a large range in

Table 7.6. Critical B concentrations in leaves of plants for the prognosis of B deficiency.

Species	Leaf and plant age or growth stage [1]	Critical B concentration or range (mg/kg)	Country; source
Bean	YFEL - 37 days after sowing	20-24	Colombia; Howeler *et al.* (1978)
Bean	YFEL - 75 days after sowing	16-18	Colombia; Howeler *et al.* (1978)
Broccoli[2]	YFEL blade when 5 % of heads formed	9-13	Canada; Gupta and Cutcliffe (1973, 1975)
Peanut[3]	Youngest open leaf at flowering	26-30	USA; Morrill *et al.* (1977)
Peanut[4]	YFEL at flowering	22-23	Thailand; Bell *et al.* (1990b)
Potato	YFEL- 7 weeks after sowing	24	Australia; Pregno and Armour (1992)
Rutabaga[5]	Youngest mature leaf blade at 5-6 leaves	37-44	Canada; Gupta and Cutcliffe (1972)
Sugar beet	Recently matured leaf blades	35-40	USA; Vlamis and Ulrich (1971)
Sunflower	YFEL- flowering	31-38	South Africa; Blamey *et al.* (1979)
Wheat	YEB- booting	3-7	Thailand; Rerkasem and Loneragan (1994)

1 YFEL - youngest fully expanded leaf blade; YEB - youngest emerged blade.
2 Critical range obtained by combining the lowest B concentrations from Gupta and Cutcliffe (1973) where leaf B was adequate for yield and absence of symptoms, with the highest values of Gupta and Cutcliffe (1975) where yield was depressed or symptoms were present.
3 Critical values for the elimination of hollow heart disorder in kernels.
4 Critical values for < 5 % hollow heart incidence in kernels.
5 Critical values for predicting the absence of brown heart disorder in roots at maturity.

the critical B concentrations required for plant production. Cereals in particular have low internal requirements for B compared to non-cereals.

Most of the critical ranges have been calibrated for sampling at the beginning of flowering. However, it should be noted that this is rather late in the growth cycle. If the crop is already deficient at this time, it will generally be too late to achieve yield potential by applying a corrective treatment. The constraint of time can be exacerbated by turnaround time between sampling and completion of the plant analysis in the laboratory. If the turnaround is more than a few days, the delay will lead to unavoidable yield losses, especially in short duration annual crops.

A selection of critical micronutrient concentrations, mostly from field calibrated studies, reported for corn, peanut, lucerne, potato and citrus species are shown in Table 7.7.

Table 7.7. Typical critical values and ranges (mg/kg) for prognosis of micronutrient deficiencies in corn, peanut, lucerne, potato and orange based on field calibration (Reuter and Robinson, 1997).

Element	Corn[1]	Peanut[2]	Lucerne[3]	Potato[4]	Orange[5]
B	10	22-23	30	24-30	20-30
Cu	5	2.1	10	5	3-5
Fe	25	32-39	-	-	36-60
Mn	15	13-15	30	20-30	16-24
Mo	0.2	0.02-0.05	0.5-0.9	0.1	0.06-0.09
Zn	15	14-20	20	19-20	16-24

[1] For the blade below and opposite the cob, sampled at tasselling.
[2] For youngest mature blade at flowering (R2 stage).
[3] Top 15 cm of shoot from vegetative plants (i.e. before flowering).
[4] For youngest mature leaf at early to late flowering.
[5] For 5-7 month old leaves sampled from healthy mature trees from the middle of non-fruiting spring extension growth.

In addition to predicting the possible deficiency of micronutrients for crop production, plant analysis can be used to diagnose existing deficiencies in plants (Smith and Loneragan, 1997). Plant analysis used in the diagnostic mode detects deficiencies that are not expressed through visible symptoms and can resolve uncertainty about the cause of symptoms. Whereas plant analysis used for the prognosis of deficiency is only a prediction of a future deficiency, given certain assumptions about the future environmental conditions and soil nutrient supply, diagnosis is based on knowledge of the internal micronutrient requirement that, in turn, should be a property of the functional micronutrient requirement in the plant.

In the case of B, for example, leaf elongation rate has been used as the basis for establishing a functional B requirement in leaves, since B is required for cell elongation.

Using this approach, Kirk and Loneragan (1988) established a functional B requirement for leaf elongation of soybean at 10-12 mg B/kg. By contrast, less than 1 mg B/kg was required for unrestricted leaf elongation of wheat (Huang *et al.*, 1996). The difference can be attributed largely to the lower cell wall B requirement in cereals than in non-graminaceous species (Bell, 1997). However, functional requirements may vary with the plant part. In wheat anthers, the functional requirement to avoid loss of pollen viability is 10 mg B/kg (Bell *et al.*, 2002). This suggests that the development of viable pollen is more sensitive to low B than is leaf growth. Indeed, in the field, sterility of wheat, which is a common problem in sub-tropical wheat growing areas of Asia, is generally found in crops that expressed no inhibition in their vegetative growth (Rerkasem, 1996a; b).

In practice, most critical micronutrient concentrations for the diagnosis of deficiencies are set not from functional requirements but based on leaf concentrations associated with maximum or close to maximum plant growth (usually 90 or 95 % of maximum growth) at a defined growth stage (Smith and Loneragan, 1997). A selection of critical concentrations developed for diagnosis of micronutrient deficiencies is shown in Table 7.8. A comprehensive listing for crops, vegetables, fruit, nut, timber and ornamental trees reported in Reuter and Robinson (1997) adds to a number of other sources of data on critical concentrations (e.g. Westermann, 1990; Jones *et al.*, 1991; Bergmann, 1992; Bennett, 1993).

The critical concentrations or concentration ranges for diagnosis of micronutrient deficiencies are typically lower than comparable values for the prognosis of a deficiency. For example, peanut leaves are diagnosed with B deficiency when levels are 10-12 mg/kg or lower. To avoid B deficiency affecting seed yield or quality, the prognostic critical value is 22-23 mg/kg. This means that, on most soils, peanut crops that contain > 23 mg B/kg in their leaves at flowering are likely to remain adequately supplied with B throughout their growth until harvest. However, leaf B > 23 mg/kg is no guarantee against a spell of dry surface soils during seed filling, which restricts B uptake and induces deficiency. Conversely, if a peanut crop contained 12-23 mg B/kg in its leaves during early flowering and experienced a severe drought that limited yield potential, no effect of B deficiency on yield would be evident. However, plants which had < 10-12 mg B/kg in expanding leaves would have been deficient, and some adverse effects on crop yield or quality would be expected.

Graminaceous monocotyledons require much lower B concentrations in leaves than other species, reflecting their low pectin levels in cell walls. Therefore, critical B concentrations for diagnosis of B deficiency are much lower in corn (Table 7.8) and wheat (Huang *et al.*, 1996) than in dicotyledonous species. By contrast, for Cu, Mn and Zn, there is a narrower range of critical values among species of widely different leaf structure and growth habit. Critical values for Fe are considered to be of limited value, since it is not total Fe in leaves that determines deficiency but rather the concentration of physiologically active Fe(II) ion. A large number of gaps exist in critical values for diagnosing micronutrient deficiencies in crops (see Reuter and Robinson, 1997) indicating that considerable research still needs to be conducted to provide for more widespread and accurate use of plant analysis.

Table 7.8. A selection of critical micronutrient concentrations or critical ranges (mg/kg) for the diagnosis of deficiencies (Reuter and Robinson, 1997).

Element	Corn[1]	Peanut[2]	Lucerne[3]	Potato[4]	Citrus spp.[5]
B	2	12	17-25	10	21
Cu	2	0.7-1.5	4-6	2	3
Fe	-	32-39	30-45	-	36
Mn	10-15	12-15	20-30	10	16
Mo	0.1	0.13	0.15-0.5	-	0.06
Zn	10-15	8-10	10-20	20	16

[1] Ear leaf sampled at tasselling to silking.
[2] For youngest mature blade before flowering except for B and Cu, which are sampled in the youngest expanding leaves.
[3] Whole shoots or upper shoots.
[4] Petiole of 5th leaf (youngest mature leaf) from growing terminal when longest tuber < 5 mm length.
[5] Healthy mature leaves of 5-7 month-old growth on non-fruiting spring shoot extension.

Species and cultivar differences in micronutrient efficiency

For all micronutrients, species vary in their response to available levels in soils (Graham, 1991). Therefore, there is scope for growing species that have low micronutrient responses to avoid the need for fertilisers. For example, lentil, chickpea and pea are more sensitive than cereals and oilseeds to Zn deficiency in India (Tiwari and Dwivedi, 1990). Among the temperate cereals, durum wheat is more sensitive to Zn deficiency than bread wheat which, in turn, is more sensitive than rye (Graham and Rengel, 1993). While species differences in response to soils low in micronutrients can be useful in managing the disorder at the farm level, more recent research has focussed on cultivar differences in efficiency to widen the scope for managing micronutrient deficiencies.

Efficient genotypes are able to acquire micronutrients from the soil more effectively and achieve higher yields than a standard cultivar (Graham, 1984). In practical terms, this means that application of micronutrient fertilisers could be avoided in some cases, or that lower amounts could be applied when growing an efficient species or cultivar on soils low in available micronutrients. In the long term, the wisdom of the strategy depends on the magnitude of the soil micronutrient reserves (Graham, 1984). If soil reserves are very large in relation to crop demand, and the primary constraint for crops is low micronutrient availability, then increased efficiency is an effective corrective strategy. It is not likely to lead to the depletion of the micronutrient content of the soil (Graham and Rengel, 1993). If on the other hand, the micronutrient deficiency is due to very low levels in the soil, then efficiency would be, at best, an interim solution.

According to Graham and Rengel (1993), breeding for nutrient efficiency in crop species is only likely to be adopted as a solution for micronutrient deficiency if the problem is difficult to solve by conventional agronomic means using fertilisers, and if the area affected is large. Hence, most resources in selecting for efficient genotypes should be focused on the major crops in a region, usually cereals. However, there is also scope for selecting micronutrient-efficient legumes (Paull *et al.*, 2005).

Conditions that justify a need for breeding to achieve micronutrient efficiency in cultivars used by growers include (Graham, 1988; Graham and Rengel, 1993):

- low availability of micronutrient in the soil,
- low sub-soil levels of micronutrients,
- prevalence of poorly recognised sub-clinical deficiencies,
- low residual values of micronutrient fertilisers,
- dry topsoil,
- low micronutrient intake in diets,
- the need to increase disease resistance, and
- the need to boost crop competiveness with weeds.

There are a number of scenarios where fertiliser and agronomic management may not be sufficient to correct micronutrient deficiencies, invoking a need for cultivar efficiency and the breeding of crop varieties for this trait.

Low sub-soil micronutrient levels are difficult to treat by conventional fertiliser application because (apart from B and Cl) most micronutrients are not sufficiently mobile in the soil and, therefore, will not leach from surface layers into the sub-soil. Some redistribution of micronutrients below the depth of placement will occur through tillage, but not enough to increase sub-soil levels. Copper in particular is strongly sorbed by the soil and does not move significantly from the point of application apart from mixing by tillage (Gartrell, 1981).

The significance of low sub-soil micronutrient levels is that low levels of Mn and Zn in the immediate soil environment limit root growth (Loneragan *et al.*, 1987; Loneragan, 1988). For those elements there is insufficient retranslocation within the plant to supply the needs to the growing root tip. Hence, low sub-soil levels of Mn and Zn impair root growth, even when the topsoil is adequately supplied with the micronutrient.

Nable and Webb (1993) also showed that wheat roots exhibited greater growth and water uptake when sub-soils were treated with Zn, and that increasing topsoil Zn could not compensate for its deficiency in the sub-soil. This is attributed to the poor retransloction of Zn within the plant and hence roots continuously need an adequate external Zn supply. Grewal *et al.* (1997) showed that Zn-efficient canola cultivars produced higher dry matter than Zn-inefficient cultivars when grown on soils with low sub-soil Zn, even though the topsoil in both cases was adequately supplied with Zn. It is expected that efficient germplasm would have increased yield potential on soils with low sub-soil levels of Zn and Mn. Unfortunately, there is insufficient data on sub-soil micronutrient levels to accurately define the target areas for introducing efficient crop germplasm.

Human and animal nutrition

An emerging concern about micronutrients in crop and horticulture nutrient management is the achievement of adequate micronutrient levels in harvested products to enhance human nutrition (Welch and Graham, 2005). Much of the research is focused on Fe and Zn levels and bioavailability in the staple cereal grains, wheat and rice. However, other crops, additional inorganic micronutrients and organic micronutrients also warrant consideration. For example, anti-nutritional components such as phytate may have a significant bearing on the bioavailability of Fe and Zn in the diet.

More recently, attention has turned to the role pre-biotic compounds such as the non-digestible oligosaccharides, e.g. inulin, that appear to stimulate Fe absorption in the colon (Yeung *et al.*, 2005). When considering human and animal diets, the range of essential micronutrients is broader than for plants, and extends to a range of organic compounds such as Vitamin A (Welch and Graham, 2005). In the context of human and animal nutrition, micronutrient levels of As, Cr, I, Se, Si and fluorine (F) also need to be considered and, for ruminants, Co is essential (Van Campen, 1991).

Three broad strategies are being pursued to boost micronutrient levels in food consumed:

- to determine how to use agronomic means, particularly soil-applied and foliar fertilisers, to increase levels found in grain;
- to determine genotypic variation and inheritability for micronutrient levels in food; and
- to determine the prospects for increasing the bioavailability of micronutrients in food products.

There is clear evidence that micronutrient levels can vary significantly in grain, suggesting that it is feasible to boost levels in grain (Welch, 1999). Supplementary applications of Zn, Cu and Mo to crops have been shown to increase levels of these micronutrients in rice and wheat grain (Duxbury *et al.*, 2005).

Additional reading

Bruulsema, T., Witt, C., Garcia, F., Li, S., Rao, T.N., Chen, F. and Ivanova, S. (2008). A global framework for fertilizer BMPs. Better Crops 92: 13-15.

Peverill, K., Sparrow, L. and Reuter, D.J. (eds). (1999). *Soil Analysis. An Interpretation Manual*. CSIRO Publishing, Collingwood.

Reuter, D.J. and Robinson, J.B. (eds). (1997). *Plant Analysis. An Interpretation Manual*. CSIRO Publishing, Collingwood.

8. Current research and development trends

New products

There is a very large range of micronutrient fertiliser products in the world but their distribution and affordability varies with geographical regions. In South Asia, for example, improvements in crop yields are being achieved by the incorporation of micronutrients in new fertiliser blends using traditional technology. In developed countries, research over the past two decades has led to the diversification of foliar fertiliser products and speciality fertiliser formulations for specific crops. New products are being considered for overcoming micronutrient disorders in aerobic rice and for reducing deleterious impacts of fertilisers in the environment.

Zinc deficiency continues to impair grain production in South Asia (Chapters 1 and 4). Presently, the best option to deliver Zn to field crops is to incorporate Zn with the macronutrient fertilisers available in the region. Accordingly, the fertiliser industry is exploring marketing zincated urea (Shivay *et al.*, 2008). A new technique for coating urea with ZnO was recently developed by Suri (2005).

The development of suspension concentrates, based on sparingly soluble inorganic micronutrient sources (Moran, 2006), is the single most significant advance in technology to occur in recent times, and it has resulted in a wide range of improved products for growers. Research continues into developing products that combine nutrients with agrichemicals, and also new surfactants and dispersants for improved flocculation and performance of products on leaf surface.

Iron deficiency remains the most difficult and expensive micronutrient deficiency to control (Fernández and Ebert, 2005), and the incidence of deficiency is increasing in rice production in particular. The use of organic materials is being tested to determine if the efficacy of current Fe products can be improved for aerobic rice (Pal *et al.*, 2008) and other crops. New chelated-Fe products are also being evaluated (Lucena *et al.*, 2008). Since EDTA has low biodegradability and persists in the environment, new biodegradable chelating agents are desirable. One that is showing some promise is imidodisuccinic acid (Lucena *et al.*, 2008).

Runoff resulting from the deployment of highly water-soluble fertilisers can reduce the environmental quality of waterways. Some governments are legislating to phase-out the use of some traditional fertilisers, including highly water-soluble phosphatic fertilisers. Gillman and Noble (2005) propose supplying nutrients on hydrotalcite and bentonite platforms for these situations. In the future, there is likely to be greater research effort into the development of alternative fertilisers with less environmental impact.

Developments in micronutrient products and research include:

- production of pelletized slow-release B from calcinated colemanite (Flores *et al.*, 2006);
- combining humic acid with B sources into a granulated product;
- incorporation of a wider range of Zn complexes or chelates into macronutrient fertilisers;
- encapsulation of water-soluble micronutrients in hydrogels and other smart polymeric materials;
- incorporation of micronutrients into polymeric phosphates (Ray *et al.*, 1997; Bandyopadhyay *et al.*, 2008);
- incorporation of micronutrients into fluid fertilisers for alkaline and calcareous soils; and
- development of crop-specific micronutrient fertiliser products.

In conclusion, although a diverse array of micronutrient fertilisers is manufactured around the world, micronutrient disorders remain problematic for many growers. Whilst there remains a need to target fertiliser development for Fe deficiency in alkaline and calcareous soils, and to develop longer lasting forms of B fertiliser, greater emphasis is required to share existing knowledge and products with growers (Chapter 4, 5, 6, 7).

Distribution of micronutrient products to small farmers

The adoption of micronutrient fertilisers by farmers has varied markedly among different countries. In Turkey, for example, within the space of 12 years, Zn fertiliser use has increased from zero to 350,000 tonnes annually. The rapid expansion in use of Zn followed several years of comprehensive research, which demonstrated large increases in yield from Zn fertiliser use, particularly in the main cereal, wheat. However, in China, despite a nationwide soil study, which demonstrated widespread problems with low microutritent levels, backed up by extensive field experiments showing crop yield increases, more than 20 years later the incidence of low micronutrient levels appeared to be unchanged (Jin *et al.*, 2006).

Many other cases can be cited, particularly in developing countries where clear evidence of the existence of micronutrient deficiencies and crop responses with high benefit:cost ratios from micronutrient fertiliser use, are not matched by widespread adoption. Questions need to be asked about the causes for failure to successfully extend the technology to farmers, and failure of the market to develop and supply products that would seem to have beneficial effects on crop production.

Small farms require small amounts of micronutrient fertilisers and, hence, there is a need to market products that meet their needs. In South Asia, for example, a small farmer may manage less than 1 ha, and if growing a pulse crop on half of the fields, she/he would need a few hundred grams of Mo fertiliser to correct Mo deficiency. Small farmers are unlikely to buy extra Mo and store it for use over a few years. Unless Mo is available in the market in quantities comparable to what the farmer needs, they are unlikely to purchase Mo.

One strategy being explored to overcome this problem in Bangladesh is to apply even smaller amounts on the seed, to further decrease the cost of fertiliser. However, the problem of supplying small quantities in the market, when needed by farmers, remains. If only 10-15 g Mo/ha is required, how can this be packaged and distributed in a profitable manner for those involved in the market chain, while still being affordable to a small farmer? When the real costs of packaging and distribution of small amounts of micronutrient fertiliser are calculated, the benefit:cost ratios estimated from experimental data are probably over-optimistic, and this may explain the market failure.

This suggests that new application, packaging and distribution strategies are needed for the reliable supply of micronutrient fertilisers into markets where there is clearly market failure, despite evidence for demand and of a substantial yield benefit. Enrichment of N, NPK or P fertilisers with micronutrient fertilisers is used in many countries. This results in more expensive NPK fertiliser, but reduces other costs of distribution and supply. It also reduces the risk to consumers of buying spurious Zn fertiliser products in unregulated markets (Shivay *et al.*, 2008). Firstly, fewer products need to be handled in the market and this makes it easier for local traders to have product in stock when needed. Secondly, it reduces the complexity for small growers using micronutrients. It cuts out the need for mixing and application of small amounts of micronutrient fertiliser.

When the NPK or P fertiliser is enriched at the correct level, alleviation of micronutrient deficiency is assured. However, it is important for advisers and traders to be aware of the likely poor results when NPK fertiliser, without micronutrient enrichment, is inadvertently supplied in the market. The strategy to use enriched NPK fertiliser will result in limited residual benefit in following crops because the amounts supplied are generally smaller than with application of micronutrients alone. Hence, the micronutrient deficiency is treated only in the crop that is fertilised, and repeated additions will be needed. On the other hand, accumulation of excess, leading to toxic levels in the soil, is minimal when micronutrient-enriched fertiliser is used.

Interaction of micronutrients with pesticides and herbicides

Herbicide use is already established as the main means of weed control in developed countries, and it is becoming more prevalent in developing countries as well. A poorly recognised aspect of herbicide use is its effects on micronutrient uptake (Osborne *et al.*, 1993). Chlorsulfuron® (from the sulphonylurea group of herbicides) decreases uptake of Zn, Cu and P by wheat. The effects are most pronounced when nutrient supply is low or marginal. With time after application, the effects of chlorsulphuron on Zn and Cu uptake diminish, due to hydrolysis of the herbicide in the soil.

On alkaline soils where chlorsulfuron has greater residual effect (Thirunarayanan *et al.*, 1985), the detrimental effects of the herbicide may be more persistent (Osborne *et al.*, 1993). The herbicide diclofopmethyl® also decreased Zn uptake by wheat (McLay and Robson, 1992). Both chlorsulfuron and diclofopmethyl decreased root length per unit weight and this decreased Zn uptake efficiency. Machota and Hopper (2001) reported that nicosulfuron® (from the sulphonylurea group of herbicides) decreased Fe uptake of maize on an alkaline soils, but not Zn uptake. The systemic organo-phosphate pesticide, terbufos®, decreased the uptake of both Fe and Zn.

Glyphosate®, the most widely used herbicide globally, appears to be antagonistic with the uptake, transport and accumulation of Fe and Mn and, to a lesser extent, with Zn transport (Eker *et al.*, 2006). The effects of glyphosate on Fe, Mn and Zn nutrition of non-target plant species needs to be considered on soils low in these micronutrients. This is attributed to the formation in the plant or in the rhizosphere of poorly soluble glyphosate-metal cation complexes.

There is also some indication that the mobility of Cu in the soil may be increased by glyphosate, particularly when glyphosate is concentrated at the soil surface after application (Barrett and McBride, 2006). Mobility of soil Zn may also be increased by the presence of glyphosate in soils, based on studies with two Chinese soils (Wang *et al.*, 2006). The implications of the increased mobility of Cu and Zn in soils treated with glyphosate for crop nutrition remain unexplored. There may also be decreased activity of glyphosate by chelation with micronutrient metals in the soil, just as the dissolution of Mn salts in a glyphosate solution diminishes the herbicide activity on target weeds (Bernards *et al.*, 2005).

Role of micronutrients in maximising benefits from high productivity land use

Cereal production globally will have to expand by 38 % in the next 20 years to meet the demand for rising world population (Surridge, 2004). In fact, this prediction may underestimate the required increase in cereal production, because it does not account for the loss of land from agricultural production due to urbanisation and transport infrastructure, the increased diversion of grains from food supply to biofuel production and the uncertain effects of global climate change on yields. Cassman (2006) estimates that cereal yields by 2025 will have to increase 59 % compared to 1995 levels to supply the rising demand for these commodities, after allowing for losses of land to biofuels, and urbanisation. Increased production can be achieved by expansion of cropped land and by higher yields.

The strategy pursued will vary depending on the opportunity. In some parts of the world, it is still possible to clear further forest for agriculture, although there are arguments (for conservation, C sequestration and watershed protection) that can be made for not doing so. Nevertheless, population expansion in parts of South-east Asia, South America and Africa is driving more people to clear forest land to seek a livelihood through crop production. In other parts of the world, where potential arable land is already largely under cultivation, or regulation of land use has reserved untapped land for conservation, water catchment and/or carbon sequestration, the only opportunity for increased production is from higher yields.

Increasing cereal yields by 59 % compared to 1995 will clearly require adjustments in micronutrient fertiliser strategies. Such yield increases are not likely without the correction of existing deficiencies. It is clear from the above discussion that there is considerable scope in many countries to increase yields by more widespread adoption of micronutient fertilisers on soils where the levels are known to be deficient.

However, large increases in crop yield will deplete plant-available micronutrient reserves in many soils to the point where deficiency becomes a limiting factor for crop production, even when it was not evident before. Moreover, in cropping systems that currently use micronutrient fertilisers on a regular basis, rates and methods of application will need to be revised to supply the increased requirements of higher yielding crops. Considerable increase in requirements for micronutrient fertiliser are predicted to allow cereal production to grow as required over the coming few decades.

Defining areas of low micronutrient status in soils

As changes occur in land use and farming systems, areas that were previously adequate in micronutrients may express deficiency with increased frequency. Similarly, areas that previously had widespread problems with low micronutrient levels may, with repeated fertiliser use, cease to be at risk of deficiency. The challenge for the fertiliser manufacturers, distributors and agronomists is to find cost-effective means to continually update information on the locations and areas affected by micronutrient deficiency so that supply can match demand and target areas of need. Rashid (2006) and colleagues have developed methods for mapping micronutrient levels in soils. However, this approach relies on having a reasonable density of sampling sites with analysed micronutrient levels. Where there is more limited soil analysis data, a different approach is required.

Wong *et al.* (2005) developed a flexible spatial modelling approach based on a weight of evidence approach for mapping risk of B deficiency. Boron deficiency risk is based on relationships between B availability and other soil or landscape properties that are more easily collected or more readily available than soil levels of micronutrients. Boron availability was predicted from established relationships between extractable soil B and the soil clay content, topsoil and sub-soil pH and geology. The latter data is commonly available spatially from soil surveys and, hence, it does not rely on the collection and analysis of large numbers of soil samples. This approach could be used to regularly update maps of micronutrient deficiencies for particular areas, and it may be a more cost-effective approach to defining where micronutrient fertilisers should be targeted.

More problematic is to define the areas where sub-soil micronutrient levels are low. The amount of data available on sub-soil micronutrients levels is too sparse for mapping to be useful. Modelling approaches, using relationships established between the available micronutrient status of the soil and soil properties such as pH, CEC and texture, which are commonly reported in soil survey documents, may be the only realistic way to define the risk of sub-soil micronutrient deficiencies, given the time and cost that would be required to sample and analyse the number of sites necessary for accurate mapping.

The link between crop micronutrient supply and human health

While crop production in the past several decades has focused on yield as its primary goal, there is increasing evidence that the focus of the future will be on farming to provide for human health and nutrition (Welch, 2001). In addition to how much yield a crop produces, it will become necessary to ask what nutritional benefit it provides. Welch and Graham (2005) argue that food production systems need to be more than just producers of carbohydrate, but also consider the levels and availability to consumers of the other essential nutrients, including micronutrients in food. Presently, over 3 billion people suffer from micronutrient malnutrition. Micronutrient deficiencies explain many deaths of children, and marginal intake of micronutrients in the diet contributes to poor learning ability and impaired growth and development of children.

Improved nutritional quality of crops produced can be achieved by agronomic methods as well as breeding strategies. Both strategies can be used to increase the micronutrient density of plant foods which, in turn, increases intake in the diet.

Increased emphasis by producers on growing grain with high levels of bioavailable micronutrients could be achieved by market-driven demand for micronutrient-dense grains. Already, there are niche markets for such grains in European and US markets (R.M. Welch, personal communication). As this market expands, grain producers are likely to seek out varieties that can satisfy the consumer demand for micronutrient-dense grain, and expect to obtain a price premium for supplying such grain into market. Such market-driven demand is less likely to influence production in developing countries than in developed countries. In developing countries, an argument can be mounted for treating the micronutrient levels in grains as a public health issue, rather than as an agricultural research issue.

If markets fail to deliver signals to farmers to produce micronutrient-dense grain, while widespread micronutrient malnutrition exists in the population, there is a powerful argument for government intervention to stimulate this development. Government regulation in Finland requires Se to be added to NPK and NP fertilisers in order to achieve a widespread increase in Se intake. This stands as a valuable case study about the benefits from government intervention to boost micronutrient levels in grain. The health benefits from increased Se in diets across the population were assessed by the government of Finland to be large enough to justify compulsory Se addition to fertilisers. The government of Turkey subsidised Zn-enriched NPK fertiliser from 1997 onwards in order to stimulate adoption by farmers. As a result, a huge increase in purchases of Zn-enriched fertilisers occured in Turkey (Cakmak, 2008b). While the benefits for public health have not been quantified, typical Zn appplication rates can increase grain Zn twofold in wheat. Since wheat is the main staple food in the diet, the flow on benefits for human health by alleviating Zn deficiency are likely to be substantial.

It is not clear whether it is preferable to offer subsidies for micronutrient–enriched fertilisers (as practised in Turkey), or to mandate micronutrient additions to fertilisers in regions where deficiency is prevalent (as practised with Se additions in Finland), or whether it is better to allow market signals to operate on supply and demand for such products. The efficacy of the policy will vary from country to country depending on how well the benefits of subsidies can be targeted and whether they cause counter-productive market distortions in supply or demand. On the other hand, mandatory additions of micronutrients fertiliser are only useful if there is no economic incentive for growers to use micronutrients.

Lack of enforced quality control opens the possibility for sales of products which fraudulently claim to be micronutrient-enriched, or possibly the use of additives that, in addition to micronutrients, contain excessive levels of unwanted elements such as Cd (see Chapter 5). However, despite the drawbacks with interventions, market failure is evident in the supply of appropriate micronutrients in many parts of the developing world, where crop productivity and human health would greatly benefit from their availability.

Interactions between micronutrient status of crops and the growing environment

Much of the micronutrient research to date has focused on deficiencies, where low soil supply or low availability in the soil accounts for the inadequate uptake by plants. However, there are several cases of more complex micronutrient deficiencies, where environmental conditions or stresses interact with the micronutrient, to exacerbate deficiency or to induce the deficiency (Moraghan and Mascagni, 1991). Relatively little research has examined such interactions, in part because the priority has been to identify and correct the simpler cases of deficiency and, in part, because the complexity of the interactions, acting in natural environments, makes it difficult to obtain research results that are easy to interpret and attribute directly to causal factors.

Boron deficiency appears to interact with light intensity, low temperature and low vapour pressure deficit in the atmosphere (Shorrocks, 1997; Bell, 1997). For diagnosis, there is little evidence yet that environmental conditions, apart from light, affect functional B requirements. Netsangtip *et al.* (1993) indicated that decreasing sunlight intensity from 70 to 35 % of full sunlight by shading, decreased B concentrations required for normal leaf elongation of black gram plants from 15 to 10 mg B/kg dry weight. Netsangtip *et al.* (1993) did not examine the possibility of differences in B distribution in mature and old leaves of the shaded and unshaded plants. Neither did their work distinguish between the possibility that the difference in the B concentration required for leaf elongation between shaded and unshaded plants was the consequence of differences in external B supply in the nutrient solutions or changes in the internal B requirements for leaf growth.

Cakmak *et al.* (1995) also demonstrated that increasing light intensity or photoperiod enhanced the effects of B deficiency on cell membrane permeability in leaf discs of sunflower plants that had been subject to B deficiency treatment for 10 days. Physiological and biochemical mechanisms by which light intensity and B deficiency interact in plants remain unknown. Marschner (1995) and Cakmak and Römheld (1997) favoured the hypothesis that high light increases phenol levels in tissues and hence increases the B required to complex with phenols.

As discussed above, several reports have linked low temperature damage in plants and B deficiency. However, because environmental factors such as low soil water, low temperature and low vapour pressure deficit act intermittently, or temporarily during the growing season, their consequences for B nutrition are difficult to predict. Since the pattern of change in leaf-B concentrations induced by unusual environmental conditions does not follow the normal pattern on which the critical values are predicted, the normal critical values may not apply in those unusual conditions (Bell, 2000).

Low soil water depresses B uptake (Hobbs and Bertramson, 1949), but its effects on critical B values are complicated by (a) when the dry period occurs, and (b) whether or not rainfall alleviates the period of drought. Noppakoonwong *et al.* (1997) found that a 30-day period of drought strongly depressed B uptake in black gram and induced severe B-deficiency symptoms, particularly pod abortion. However, in that particular field experiment, rainfall occurred during the mid-pod setting period so that, as B uptake increased with increasing soil water content, pod setting resumed and largely compensated for the loss of pods that occurred during the dry period. Critical B concentrations for prognosis in that season declined from about 30 mg B/kg before flowering to 9 mg B/kg during the period of drought and increased again for leaf samples collected after the drought period. By contrast, Bell *et al.* (1990b) reported that, in irrigated black gram grown on similar soils in the same environment, the critical B concentration in YFEL for the prognosis of B deficiency declined from about 45 mg B/kg before flowering to 20 mg B/kg during late pod setting. The differences between the two sets of results only serve to illustrate that a critical value for prognosis is a prediction of the possibility of a deficiency occurring for yield.

One of the major difficulties with B-deficiency diagnosis and prognosis is that environmental factors such as low soil water, low temperature, high light and low vapour pressure deficit can induce a temporary B deficiency. Better definition of the effect of each of these environmental stresses on B response is needed in the first instance. However, prediction of the risks of B deficiency in these cases may also be improved by measuring relevant environmental data (Rawson, 1996).

Zinc deficiency also appears to interact with environmental stress, including drought, high temperature, and high light intensity (Cakmak, 2008b). Under high light intensity, there is greater development of Zn-deficiency symptoms on plants (Cakmak, 2008b). This is attributed to the greater production of reactive oxygen species (ROS) under high light intensity, and to the role of Zn in protecting cells from ROS. According to Cakmak (2008b), greater evidence of Zn deficiency under dryland conditions than in well-watered plants can often be attributed to the greater levels of ROS in plants suffering drought and heat stress. Under these conditions, Zn supply can protect plants against photo-oxidative damage.

Micronutrient-efficient cultivars

Efficient cultivars were shown in many studies to outyield standard cultivars when grown on soils low in one of more of the micronutrients. Among released cultivars for a range of crops, there are many reports of screening studies to rank cultivars according to uptake efficiency on soils with low micronutrient levels (e.g. Singh *et al.*, 2004 for peanut; Paull *et al.*, 2005 for legumes). However, internationally, there are relatively few examples of breeding programmes set up to introduce micronutrient efficiency into adapted germplasm that lead to new cultivars that are widely adopted by farmers.

By contrast, there are many examples of newly introduced cultivars which fail across large areas of the target region for release due to micronutrient use inefficiency (e.g. Srivastava *et al.*, 2000 for B deficiency in lentil). According to screening trials conducted by Rerkasem and Jamjod (2001), 90-100 % of the CIMMYT bread wheat and durum wheat germplasm in the nursery was B-inefficient. Therefore, for the large areas of South Asia, where wheat is grown on low-B soils, this germplasm often fails. Ahmed *et al.* (2002) screened 37 released varieties of advanced breeding lines of wheat from Bangladesh and found that all were B-inefficient. However, low-B soils are widespread in the country and, hence, sterility in wheat remains a significant yield-limiting factor for farmers.

The resources needed to breed a micronutrient-efficient cultivar are substantial and require a long-term commitment. It is unlikely that such breeding programmes can be mounted for all crops grown in an area. The priority for such research should be devoted to the main staple foods, usually cereals. Further, before embarking on a breeding programme, greater consideration needs to be given to the pre-conditions outlined by Graham (1988) for justifying such a programme.

Considering the large number of combinations of crop species and micronutrient deficiencies, it is not surprising that few combinations have been investigated in terms of nutrient efficiency mechanism(s) and in establishing the physiological and genetic control of the efficiency. However, according to Paull *et al.* (2005) it is probable that similar patterns with respect to efficiency for specific nutrients will emerge across crop species, and, in particular among the more closely related genera. For example, Fe efficiency of both chickpea and lentil is controlled by major dominant genes.

Understanding the physiology, genetics and regional distribution of efficiency for a particular nutrient in one crop should not only assist in developing nutrient-efficient varieties for that crop, but also for other crops. A number of studies also indicate that efficient lines of species originate from regions where the low micronutrient soils are prevalent. For example, lines of chickpea and lentil from West Asia commonly exhibit Fe efficiency, while lines from India and Pakistan tend to be inefficient (Ali *et al.*, 1988 ; Materne *et al.*, 2002). Such broad regional differences in efficiency can speed up the process of identifying efficient germplasm for screening and for introducing micronutrient-efficient germplasm to breeding programmes.

Planning for the future

Best-management practices for micronutrients in different farming systems need to continually evolve to allow for changes in the system, especially changes in inputs and outputs. Progressive increases in crop yields through improved varieties and agronomic advances are common in many farming systems. Unless micronutrient supply increases with increases in crop removal, deficiencies may emerge where they did not previously limit crop growth.

Continued use of micronutrients, without regard to nutrient budgets, may lead over time to the accumulation of excessive levels that threaten food safety or environmental quality. Changes in tillage practices (e.g. zero tillage), herbicides used and cultivars can also trigger the emergence of micronutrient deficiencies in farming systems where they did not previously exist.

Emerging cropping systems, such as rice-maize rotations and water-saving rice production technologies, which are likely to spread rapidly in Asia, will require a re-examination of micronutrient supply for productive and sustainable cropping. Declining availability of water for rice production is expected to trigger the emergence in Asia of new water-saving cropping patterns such as rice-maize rotations, aerobic rice and water-deficit irrigation for rice. Water-saving rice production technologies involve soil water regime changes compared to flooded rice, and changes in micronutrient availability are expected.

In the aerobic rice system, rice is flood irrigated every 4-7 days resulting in cycles of soil saturation followed by drainage. In the water-deficit irrigation system, water levels are maintained between the soil surface and 20 cm depth. Gao *et al.* (2006) reported that Zn uptake was depressed in aerobic rice *vs* paddy rice on an alkaline soil of north China, suggesting the need for increased Zn fertiliser in this cropping system relative to double or triple cropping paddy rice. The further spread of water-saving technologies for rice production areas may require significant revision to existing micronutrient fertiliser programmes.

Organic agriculture is an emerging food production system that has been growing rapidly over the past decade or more. While synthetic fertilisers are commonly excluded from organic agricultural systems, micronutrient fertilisers are allowed if there is evidence of deficiency (e.g. NASAA, 2004). At this time, there are no micronutrient products on the market that have been developed for organic crop production, but specified inorganic micronutrient products are acceptable for use. The optimal supply of micronutrients in organic production systems has rarely been considered, but may attract more attention, especially with the rise in concern about micronutrient levels in food for enhanced human nutrition.

The future supply of micronutrients to agriculture and horticulture needs to recognise the increasing public scrutiny of food safety and environmental quality. Pro-active industry programmes are needed to ensure that the skills and knowledge of all individuals involved in the supply and distribution of micronutrients (and other nutrients) promote environmental stewardship, occupational health and safety, food safety and agricultural profitability (AFSA/FIFA, 2006).

The Fertcare scheme in Australia (AFSA/FIFA, 2006) is an example of a national industry scheme that provides training and accreditation for all fertiliser and soil ameliorant industry businesses and staff. It is designed for all those involved in importing, manufacturing, storing, handling or distributing fertilisers; fertiliser sales staff dealing with customers; or agronomists and advisers providing recommendations for fertiliser use. The intended outcome of this initiative is to ensure that farmers Australia-wide receive consistent quality advice for fertiliser and soil ameliorant handling and use, which will, in turn, benefit the industry and the Australian community. Similar programmes would be valuable in other countries to ensure that the industry is pro-actively dealing with potential risks to the future use of micronutrients for productive, safe and sustainable agriculture, forestry and horticulture.

The growing importance of micronutrients in agriculture, horticulture and forestry necessitates comprehensive programmes to train human resources in each country. As discussed above, training is needed at all strata of the industry. Clearly, the capacity to mount such training programmes is greater in developed countries than in most developing countries. Universities play a key role in developing capacity for training, providing advice to growers and conducting research, which allows continual improvement of BMPs. This process is greatly facilitated by the improved access afforded by the internet, to knowledge about micronutrients from almost anywhere in the world.

The rapid development of research capacity and outputs in the molecular biology of micronutrients is generating important new understanding of the role of these elements in plants. Also, there is a potential to transform plants for improved micronutrient status. In addition, there remains the need to maintain and develop skills in understanding the physiology of micronutrients in plants. Equally important is the need to obtain a better understanding of the chemical reactions of micronutrients in soil, as well as the biogeochemical cycling of micronutrients in diverse agricultural, horticultural and forest (including plantation forests) systems.

Additional reading

AFSA/FIFA (2006). *Fertcare Handbook*. Australian Fertiliser Services Association (AFSA) and Fertilizer Industry Federation of Australia (FIFA), Melbourne.

9. Micronutrient market

Consumption of micronutrients accounts for less than 1 % of the global fertiliser volume but, nevertheless, the essential and specific roles of micronutrients can be a key determinant of crop yields and quality. Research has identified soils, crops and environmental conditions that can induce micronutrient deficiencies or toxicities (see Chapters 2, 4 and 7), and this body of information, which is briefly summarized below, is the basis for predicting the micronutrient market potential.

Factors affecting micronutrient market potential

Micronutrient availability in the soil and uptake by crops is strongly dependent on soil types and properties (Table 9.1).

Table 9.1. Generalised relationships between soil types and properties and micronutrient deficiencies (Alloway *et al.*, 2008b; c). See Chapter 2 for more detailed discussion of the effect of soil properties on micronutrient availability.

Soil type/ properties	Deficient micronutrient(s)
Sandy textured and strongly leached soils	B, Cl, Cu, Fe, Mn, Mo, Zn
High soil pH (>7)	B, Cu, Fe, Mn, Zn
High $CaCO_3$ content (>15 %); calcareous soils	B, Cu, Fe, Mn, Zn
Recently limed soils	B, Cu, Fe, Mn, Zn
High salt content	Cu, Fe, Mn, Zn
High organic matter content (>10 % OM)	Cu, Mn, Zn
Acid soils	Cu, Mo, Zn
Heavy clay	Cu, Mn, Zn
Gleys	Zn

Crops differ in their susceptibility and response to micronutrients. A number of plant factors influence the sensitivity of crops to micronutrient deficiencies. These factors include: plant genoptype; the volume and length of roots and rooting conditions; root-induced changes in the rhizosphere pH; mycorrhizal infection (that increases the effective root surface area); the secretion of root exudates such as phytosiderophores; pathological diseases; the efficiency of utilization of the micronutrients once absorbed; and the crop sequence since residues of some plant species may render some micronutrients less available in the soil (e.g. Cu deficiency in wheat after oilseed rape) (Alloway, 2008b).

Changes in environmental conditions above ground and in the soil often have a greater effect on micronutrient than on macronutrient status of crops. There are a number of growing conditions and root factors that can induce micronutrient deficiencies. Nitrogen supply affects the growth rate and the elements incorporated in the proteins contained in leaves, and it can cause dilution of the micronutrients. Similarly, phosphate supply can contribute to the dilution of micronutrients. Furthermore, it can inhibit mycorrhizal infection and affect the bioavailability of Zn. Moisture, temperature and light intensity are other factors that can induce micronutrient deficiencies. For instance, availability of B and Cu is greatly affected by low soil moisture that results in deficiencies being more prevalent during dry seasons, while Mn deficiency is aggravated by cold wet weather conditions (Moraghan and Mascagni, 1991). The application of some agrichemicals can also have an impact (e.g. glyphosate-induced Mn, Zn and Fe deficiencies). There are also antagonistic effects among micronutrients such as the interactions between Cu and Zn and between Fe and Mn.

A generalised ranking of crop susceptibility to micronutrient deficiencies is summarized in Table 9.2. In most instances, cereals are not very sensitive to B deficiency, but commonly require Cu, Fe, Mn and Zn. Most vegetables, particularly leafy vegetables and *Brassicas* are highly sensitive to B deficiency, while soybean, sugar beet and tomato are sensitive to Fe, Mn and possibly Mo deficiencies, and fruit crops are sensitive to Mn deficiencies. The majority of crops can be affected by Zn deficiency with maize, beans and citrus being highly sensitive. Rice and wheat are two major staple food crops in many countries, and Zn deficiency has been known to significantly affect their yield worldwide, although they are recorded to have low to medium sensitivity. While a generalised ranking of crop species is a useful first approximation of micronutrient deficiency risk, each species may express large genotypic variation in micronutrient efficiency. For example, soybean generally has low susceptibility to B deficiency, but the cultivars used by Rerkasem *et al.* (1997) in northern Thailand were responsive to B fertiliser addition.

The relative importance of micronutrients to crop production has been assessed in various countries (Table 9.3). In countries where intensive agriculture is practised, micronutrients are added as preventive measures and for higher yields.

Zinc is the most prevalent micronutrient deficiency, with extensive deficiency registered in most of the countries listed, apart from a few exceptions in Europe. The countries and regions where Zn deficiency is an important problem are those with lowland rice production, semi-arid areas with calcareous and/or alkaline soils, or where crops are grown on highly weathered and leached soils such as tropical red soils and Podzols, or other types of soil from sandy parent materials (Alloway, 2008a). India, Iraq, Italy, Korea, Pakistan, Syria and Turkey have extensive Zn deficient areas.

The world's largest known area of wheat affected by B deficiency is in the contiguous upland cereal growing areas of India, Nepal and Bangladesh (Rerkasem and Jamjod, 2004). On the other hand, toxic B levels can be found in various low rainfall areas of the world, specifically in southern Australia, some parts of India, and East Asia (Alloway, 2008b). Boron deficiencies in the USA occur on soils with low organic matter, low pH and sandy and silt loams, particularly in the southern Atlantic and Pacific states

Table 9.2. Crop sensitivity/susceptibility to micronutrient deficiencies: (H-high; M-medium; L-low, - unknown/no data). Compiled from various sources: Alloway (2008b; c); Shorrocks (1991b); New Ag International (2003; 2007); IFA (2008); inputs from IFA member companies.

	B	Cu	Fe	Mn	Mo	Zn
Cereals						
Barley	L	H-M	H-M	M	L	M
Maize (corn)	M-L	M	M	L	-	H
Oats	L	H	M	H	M-L	L
Rice	L	H	M	M	L	M
Rye	L	L	L	L	-	L
Sorghum	L	M	H	H-M	L	H-M
Wheat	L	H	M-L	H	L	M-L
Fruits						
Apple	H	M	-	H	L	H
Citrus	L	H	H	H	M	H
Grapes	H	M	H	H	L	L
Vegetables						
Beans	L	L	H	H	M	H
Broccoli	H	-	-	M	M	-
Cabbage	H	M	M	M	H-M	-
Carrot	M	H	-	M	L	L
Cauliflower	H	-	-	M	M	-
Lettuce	M	-	-	M	M	-
Pea	L	M-L	M	H	M	L
Potato	L	L	-	H	L	M
Spinach	M	H	H	H	H	H-M
Tomato	H-M	M	H	M	M	H-M
Other crops						
Alfalfa	H	H	M	M-L	M	L
Clover	M	L	-	-	-	M
Cotton	H	M	M	M-L	-	H
Grass	L	L	H	M-L	L	L
Linseed/flax	M	-	H	L	-	H
Oilseed rape/ canola	H	L	-	-	H	M
Soybean	L	L	H	-	H	M
Sugar beet	H	M	H-M	M	M	M
Sunflower	H	H	-	-	-	-

(Martens and Westermann, 1991). Boron deficiency is found in calcareous soils of the north and in acid soils of southern China. In northern China, Zn deficiency is more prevalent on account of alkaline soils (Alloway, 2008a).

Table 9.3. Countries with identified micronutrient deficiencies and the relative importance of the micronutrient: ●● very important; ● important; N-not important; na-not available (Shorrocks, 1991b; IFA, 2008; inputs from reviewers/IFA member companies).

		B	Cu	Fe	Mn	Mo	Zn
Europe	Denmark	●	●	N	●●	N	N
	Finland	●●	N	N	●●	N	●
	France	●	●	●	●	na	●●
	Germany	●●	●	N	●●	●	●
	Hungary	N	●	N	●	●	●
	Ireland	na	●●	na	●●	na	● ●
	Italy	●	●	●●	●●	N	●●
	Netherlands	N	●	N	●	●	N
	Norway	na	v	N	N	●	na
	Poland	●●	●●	N	●●	●●	●●
	Romania	●	N	●	N	●	●●
	Scotland	na	●●	na	na	na	na
	Spain	●	na	●●	na	na	na
	Sweden	●	N	N	●●	na	N
	United Kingdom	●	●	●	●●	●	N
Americas	Argentina	●	na	N	N	●●	●●
	Brazil	●	●●	N	●●	●	●
	United States	●●	●●	na	●	●	●
Africa	Morocco	●●	●	●	●	N	●●
	South Africa	●	●●	na	na	na	●●
Asia	China	●●	N	●●	●●	●●	●●
	India	●●	na	●●	N	N	●●
	Iran	●	N	●●	●●	N	●●
	Philippines	●	na	na	na	na	●●
	Saudi Arabia	na	na	●	na	na	na
	Turkey	●	na	N	●●	N	●●
	Vietnam	●	na	N	●●	N	●●
Oceania	Australia	●●	●●	●	●●	●●	●●
	New Zealand	●	●●	N	N	●●	na

In Ireland and Poland, about 40 % of the total cropped area is deficient in Cu (based on soil analysis) due to the widespread occurrence of sandy and calcareous soils and intensive cropping. There are about 9 million ha deficient in Cu in western and southern Australia and in western Victoria. Copper deficiency is not a problem in most Asian countries (Alloway, 2008b). A study commissioned by the International Copper Association (ICA) reported that, in Europe, about 12 million ha of cropland, including soils under permanent grasslands, rough grazing and wilderness, are either currently deficient or have a high risk of developing Cu deficiency (New Ag International, 2007).

Mediterranean-type soils of the Middle East are highly deficient in Fe due to the high-pH calcareous soils. Southern Europe and North America are well-established Fe fertiliser markets. With the development of new methods of detecting deficiencies, South America, parts of Africa and East Asia are potentially large markets.

Manganese deficiency is widespread in northern Europe, particularly in Sweden and the UK, with their relatively cool, higher rainfall, temperate climates.

Molybdenum deficiency is likely to occur in acid and severely leached soils. Australia, Africa, the USA and China are known to have significant Mo deficiency problems in a number of crops, particularly in *Brassicas* and legumes.

In northern Europe, the predominantly acid soils are likely to result in Cu, Mo and Zn deficiencies, but there are large areas of neutral to alkaline soils where Mn is deficient. There are significant areas deficient in Fe in southern Europe and in areas bordering the Mediterranean Sea.

The patterns of use of micronutrients in the USA are changing rapidly, and over the past 5 years there has been a significant growth in micronutrient application across US agriculture and important changes in the manner in which fertilisers are used. Important drivers for this change include an increasing demand for high quality and uniform product, changing agricultural practices and increasing intensification including precision agriculture, low-till management, and the use of genetically modified crops (Brown, 2008). Averaged across the entire USA, Zn accounts for ca. 45 % of all micronutrient use, Fe 25 %, B 20 %, Mn 8 % and Cu 2 % (www.tfi.org). The greatest Zn use is on corn and soybean in the central states. The most significant consumption of Fe, B and Cu occurs in the Pacific region (alkaline soils; horticultural crops). One of the most significant trends in the USA is the dramatic increase (almost 300 %) in the use of Mn, Fe, Zn and to a lesser extent B over the past 5 years in the primary soybean/corn growing states.

South America has the largest potential land area to expand food, feed, fibre and biofuel production and generally favourable climatic conditions, but soils are often acidic and infertile, in particular in Brazil. Zinc deficiency is the most widely reported, although Cu, B, Mn and Fe deficiencies are also found, mostly in Oxisols and Utilsols (Fageria and Stone, 2008).

In China, large areas are affected by micronutrient deficiencies. It is estimated that more than one third of the country's farmland area has soil Zn, Mo or B levels below critical levels (Table 9.4).

Table 9.4. Micronutrient deficient soil areas in China (Lin and Li, 1997, cited from Zuo *et al.*, 2008).

	Estimated deficient land area (below critical level)		
Nutrient	Critical level (mg/kg)	Area (million ha)	Total farmland (%)
Zn	0.5a	48.6	51.1
Mo	0.15c	44.5	46.8
B	0.5b	32.8	34.5
Mn	5.0a	20.3	21.3
Cu	0.2a	6.5	6.9
Fe	4.5a	4.7	5.0

Extractants: a= DTPA; b= hot water; c= NH_4Acetate.

Indian agriculture is not susceptible to deficiencies of Mn, but problems with low soil Zn, B and Fe are very extensive and have become more widespread in recent decades. Based on soil and plant analysis, Singh (2008) reported that 49 % of the Indian soils were potentially deficient in Zn, 33 % in B, 12 % in Fe, 11 % in Mo, and 3 % in Cu. In Bangladesh, an estimated 2 million ha of land was reported to be Zn-deficient (White and Zasoski, 1999).

In Australia, Mo deficiency is most widespread in acid soils, while Zn deficiency is most widespread on alkaline soils. Zinc remains the most important micronutrient in Australian agriculture (Holloway *et al.*, 2008), and its importance is increasing due to the intensity of production and the shift away from the Zn-enriched superphosphates. It is estimated that about 8 million ha of cultivated land is affected in western Australia.

Soils in Africa are dominated by arid, young soils or highly weathered old soils. Some 15 % of the continent's soils are acidic (Table 9.5), and it is in these soils that most of the agricultural production is concentrated (van der Waals and Lakes, 2008). Micronutrient deficiencies in Africa are considered widespread. Information on micronutrient deficiencies in Africa is available mostly for cash crops, but it is usually lacking for staple crops. There is a need for governments in these countries to facilitate research into the real extent of micronutrient deficiencies in staple crops, as well as their impact on human health (van der Waals and Lakes, 2008).

Table 9.5. Soil pH ranges and area covered in Africa (Eswaran *et al.*, 1997).

Soil pH range	Area (x 1,000 km^2)	Percentage of total
<3.5	31	0.1
3.5 – 4.2	1193	3.9
4.2 – 5.5	3278	10.7
5.5 – 6.5	4306	14.0
6.6 – 8.5	6997	22.8
> 8.5	14845	48.4

Micronutrient consumption

The market for micronutrients is small and competitive. It involves a few large manufacturers/producers of single micronutrient types and many small to medium-size formulators of multi-micronutrient mixes and finished products. Due to the large diversity of micronutrient fertiliser types and to the structure of the market, it is difficult to gather and analyse micronutrient consumption data. Furthermore, consumption data are not reported on a nutrient basis, with the exception of a few countries. Since country data, when available, are generally estimates, it is difficult to generate a "realistic" picture of the global micronutrient fertiliser market.

According to various sources, worldwide micronutrient consumption in 2006 is estimated at some 700,000 metric tonnes (t), with the Asian market capturing 64 % of the total (Fig. 9.1). The global market for chelated micronutrients would amount to some 40,000 t. The largest markets for chelated fertilisers are Europe and North America, and Fe chelates account for 50 % share of this (Fig. 9.2). Zinc sulphate is the most commonly used Zn source, particularly in the Asian market, where price is the main consideration in the product choice. Demand for chelates, which are more expensive (per kg of product notwithstanding their lower application rate and sometimes higher benefit:cost ratio), is low in Asia. In recent years, there has been growth in products based on formulated zinc oxide, particularly in Europe and the USA.

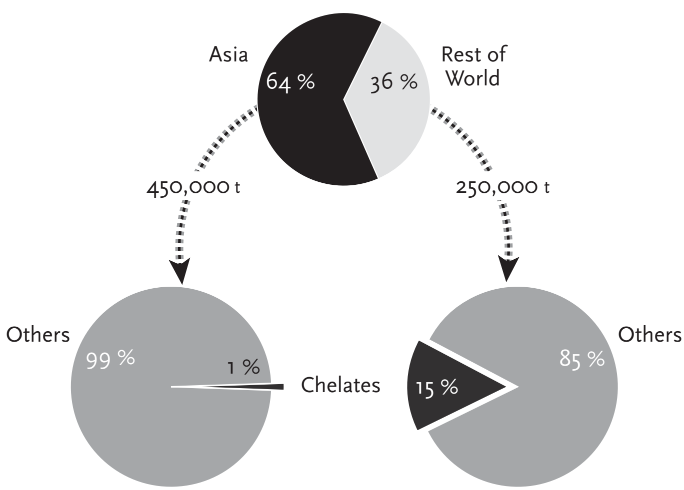


Figure 9.1. World micronutrient market in 2006 (personnal communication from Akzo Nobel, SQM and IZA).

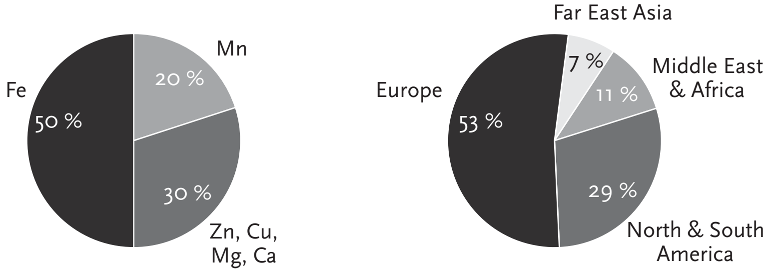


Figure 9.2. World market for chelated micronutrients in 2006 (personnal communication from Akzo Nobel, SQM and IZA).

The USA accounts for about 25 % of world B production, and it is considered the largest domestic market for this micronutrient, even though 50 % of the production is exported. However, in 2001, only 4 % of the overall B market in the USA was for agricultural use; the rest was used in the glass and ceramics industries. Other producers of B are China, Chile, Turkey, Argentina and Russia (New Ag International, 2003).

In 2005, 8,000 to 10,000 t of Mn chelates (mainly EDTA) were sold worldwide, and about 200,000 t of Cu sulphate was used, mainly for plant protection (fungicides), with possible additional tonnages to treat Cu deficiency in broad-acre and cash crops (New Ag International, 2007).

Consumption of micronutrient fertilisers in selected countries is given in Table 9.6.

Table 9.6. Micronutrient consumption (t) in selected countries in 2006 on a nutrient (N) or product (P) basis. Data sources: USA - AAPFCO and TFI (2006); Brazil - Rocha (2006); IFA (2008). Australian data does not reflect values from bulk-blends and mixed with NPKs.

Country	B	Cu	Fe	Mn	Zn
Australia	1929(N)	1029 (N)	na	1320 (N)	3961 (N)
Brazil	8100 (P)	10800 (P)	na	21600 (P)	21600 (P)
India	10000 (P)	na	8000 to 10000 (P)	na	120000 (P)
Italy	700 (N)	na	11000 (P)	na	na
USA	14479 (P)	9076 (P)	31299 (P)	8750 (P)	59342 (P)

In Brazil, the consumption of micronutrients declined significantly in 2006 compared to 2004 (Fig. 9.3) contrary to the consumption trend observed in the USA (Fig. 9.4).

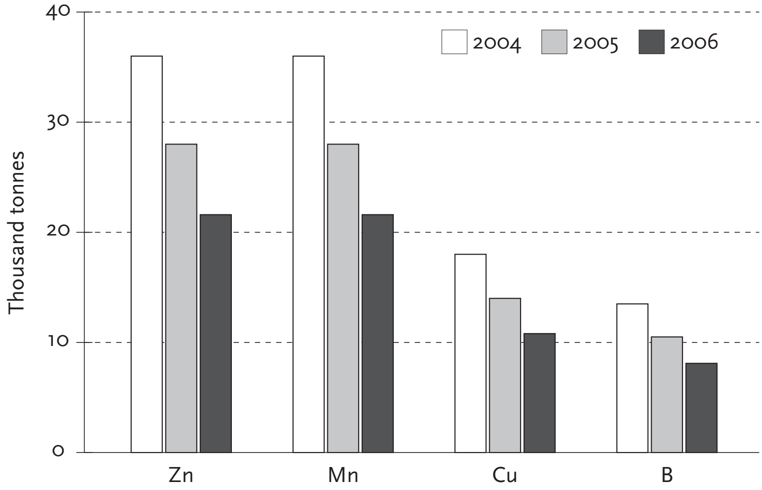


Figure 9.3. Micronutrient consumption in Brazil in 2004-2006 (Rocha, 2006).

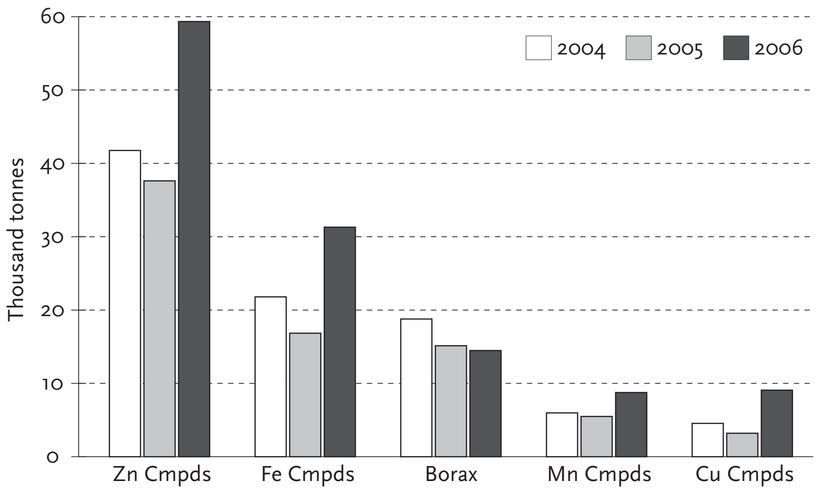


Figure 9.4. Micronutrient compounds (Cmpds) consumed in the USA over the period 2004-2006* (AAPFCO and TFI, 2006).
* *Year ended June 30*

Potential market

From information on countries and crops affected by micronutrient deficiencies, a rough estimate of the market potential can be calculated (Table 9.7) using the percentages of micronutrient deficient agricultural soils in the world.

Table 9.7. Potential micronutrient deficient cropped areas in the world. (Sillanpää, 1990, cited from Graham, 2008 and IFPRI, 2000; based on annual cropland in the world of 1.38 billion ha of which 91 % (1.255 billion ha) is under annual crops and the remaining 9 % under perennial crops.

Micronutrient	Deficiency in world's agricultural soils (%)	Potential area – annual crops (million ha)	Potential area – perennial crops (million ha)	Total potential area (million ha)
Zn	49	614	64	678
B	31	389	41	430
Mo	15	188	20	208
Cu	14	175	18	193
Mn	10	125	13	138
Fe	3	37	4	179

A survey of micronutrient fertiliser use was conducted by IFA in 2008, and the results are summarized in Table 9.8. The need for specific micronutrients is largely explained by the major soil types in the country. Reports suggest that direct use of micronutrients to treat deficiency (often sprayed in combination with agrochemicals) and as additives to NPK products are the most common uses of micronutrients in almost all the countries that responded. Generally, it can be concluded that there is still a need for more specific information on the benefits, costs and economic return associated with micronutrient use, as well as on the need for timely and reliable advice for determining deficiencies.

Most developed countries that have the facilities and resources to detect micronutrient deficiencies in crops and soils have an advantage over developing countries in alleviating deficiencies in crop production. Many developing countries in Asia, the largest market for micronutrients, still lack the ability to determine in a timely manner, deficiencies of many micronutrients.

Table 9.8. Partial results of the micronutrient fertiliser use survey outlining the current situation in the international micronutrient market (IFA, 2008).

	Identified micronutrient deficiencies	Micronutrient deficiency maps	Main micronutrient sources	Main crops affected by micronutrient deficiencies	Common micronutrient uses	Constraints to micronutrient use
Argentina	B, Cl, Mo, Zn, Co	none	- oxisulphates of Zn, Mn and Cu - ulexite, colemanite - sulphates of Zn, Cu, Fe and Mn - chelates of Zn, Cu, Fe and Mn - Na and ammonium molybdate	- soybeans-Mo and Co (10 % of cropped area) - wheat-Cl (2 %) - apple and pears-B (15 %)	- direct use (B) - fertigation (several) - seed treatment (Co and Mo) - raw material in bulk blends	- lack of information
Australia	B, Co, Cu, Fe, Mn, Mo, Zn	Small scale for Zn, Cu and Mo. B map for W. Australia	- Zn oxides and sulphates - Cu sulphate and oxychloride - borax - Fe, Zn, Cu chelates and oxide - Mo trioxide	na	- direct use - raw material - additive - fertigation - hydroponics - seed treatment	- confidence in predictive method and economic return
Brazil	B, Mn, Cu, Zn	none	- oxisulphates of Zn (50 %), Mn (30 %), and Cu (10 %) - B (10 %)	na	- raw material - additive - seed treatment	- availability - price - lack of information
China	B, Mn, Mo, Cu, Fe, Zn	yes-B, Cu, Fe, Mn, Mo, Zn	- Zn, Mn, Fe, Cu sulphates - ammonium molybdate; - borax, Na borate	- rice and maize-Zn - fruit-Fe - soybeans-M - rapeseed-B	- direct use - raw material - additive - seed treatment	- availability of products - lack of information
Egypt	B, Cu, Fe, Mn, Zn	yes-Cu, Fe, Mn, Zn	- borax - chelates and sulphates	- citrus-Zn, Mn, Fe - mango-Zn, Mn, Fe - rice-Zn - grapes-Fe, Zn, Mn - cotton-Mn, Zn, Fe - wheat-Zn, Fe, Mn, - maize-Cu, Zn, Fe, Mn - olives-Zn, Fe, Mn, B	- direct use - raw material or additive	- price - lack of legislation - lack of information

	Identified micronutrient deficiencies	Micronutrient deficiency maps	Main micronutrient sources	Main crops affected by micronutrient deficiencies	Common micronutrient uses	Constraints to micronutrient use
Germany	B, Cu, Fe, Mn, Mo, Zn	none	na	na	- direct use - raw material - additive to other fertilisers	- lack of information
India	B, Zn, Fe	yes-Zn	- sulphates of Zn, Fe - borax - mixtures	- rice-Zn	- direct use - raw material - additive - fertigation	- lack of information
Iran	B, Cu, Fe, Mn, Zn	yes-B, Cu, Fe, Mn, Zn	- sulphates of Zn, Fe, Mn and Cu - Fe chelates - boric acid	na	- direct use - raw material - additive	- price
Italy	B, Cu, Fe, Mn, Zn	none	- chelates of Zn, Mo, Mn, Fe - copper oxychloride - boron ethanolamine - boric acid	- pear-Fe - olive-B - maize-Zn - kiwi-Fe	- direct use - raw material - additive	- price
Japan	na	na	na	na	- raw material - additive	- lack of information
New Zealand	B, Cu, Mo, Co, Se	yes- Co, Se	- Zn sulphate/oxide - Na molybdate - sulphates of Cu and Co - Na borate - Na selenate	na	- direct use - raw material - additive - animal health	- none
Poland	B, Cu, Mn, Mo, Zn	yes-B, Cu, Mn, Mo, Zn	- Cu, Mn, B, Mo and Zn-popular brands in the market (not specified)	na	- direct use - raw material - additive - fertigation - hydroponics - seed treatment	- price

	Identified micronutrient deficiencies	Micronutrient deficiency maps	Main micronutrient sources	Main crops affected by micronutrient deficiencies	Common micronutrient uses	Constraints to micronutrient use
South Africa	B, Fe, Zn	none	- Fe and Zn EDTA - Solubor®	na	- direct use - fertigation - hydroponic	- price - lack of information
Turkey	Fe, Mn, Zn	yes-Cu, Fe, Mn, Zn	- mixed in NPK - Zn sulphate, Zn oxide	na	- direct use - raw material - additive - fertigation	- price - lack of information
United Kingdom	B, Cu, Fe, Mn	na	- salts and chelates of Mn, Fe, Cu - Solubor®, borax	na	- direct use	- none
Vietnam	B, Mn, Zn,	none	- Zn sulphate, chelates - boron	- coffee-Zn	- direct use - raw material - additive	- availability of products - price

Terminology used in Table 9.8:
Direct use - direct application of micronutrient products to correct or prevent deficiency;
Raw material - mixed or blended with other micronutrient sources to come up with a "new formulation" used for soil or foliar application as the main micronutrient source;
Additive - added to NPKs or agrochemicals to fortify or enrich the major product with some micronutrients.

Additional reading

Alloway, B.J. (2008b). Micronutrients and crop production: An introduction. p. 1-39. In B.J. Alloway (ed.), *Micronutrient Deficiencies in Global Crop Production*. Springer, Dordrecht.

Graham, R.D. (2008). Micronutrient deficiencies in crops and their global significance. p. 41-61. In B.J. Alloway (ed.), *Micronutrient Deficiencies in Global Crop Production*. Springer, Dordrecht.

Sillanpää, M. (1990). *Micronutrient Assessment at Country Level: An International Study*. FAO Soils Bulletin No. 63, FAO, Rome.

Welch, R.M., Allaway, W.H., House, W.A. and Kubota, J. (1991). Chapter 2. Geographic distribution of trace element problems. p. 31-57. In J.J. Mortvedt, F.R. Cox, L. M. Shuman and R.M. Welch (eds.), *Micronutrients in Agriculture*, 2nd ed. SSSA Book series No.4. Soil Science Society of America, Madison, Wisconsin.

10. Policy and regulatory context of micronutrient use

Agriculture and food policies

Although the role of micronutrients in crop production is well researched, their use is limited in many potential markets due to lack of information and low confidence levels in the prediction of deficiency(ies) and in the economic returns from micronutrient fertiliser use (IFA, 2008).

Nutrients enter the human food chain mostly through the agricultural system. Through agricultural policies, governments can influence agricultural productivity, farming practices and food quality (Welch, 2008). In addition to food security goals, policy makers should take into account human nutrition for good public health in making agricultural policies, taking into consideration what is good for the consumers and what is profitable for the farmers. Unfortunately, optimising the nutrient content of food products through appropriate farming practices has never been an objective of agricultural or health policies, notwithstanding its potential to effect large gains in public health (Welch, 2008).

The most important micronutrients essential for humans, crops and livestock are B, Co, Cu, Fe, Mn, Mo and Zn (Table 10.1). Zinc and Fe have been identified as the most-commonly deficient micronutrients in both humans and crops. They rank fifth and sixth, respectively, among the ten leading causes of illness and disease in humans, specifically in low-income countries (WHO, 2002). It is generally observed that the regions of the world with Zn-deficient soils are also characterised by widespread Zn deficiency in humans (Cakmak, 2008b; c).

To reverse the increasing malnutrition and "hidden hunger" trend, food fortification or micronutrient supplementation for humans is being carried out, but these are costly programmes. Other solutions being worked on are plant breeding strategies (i.e. genetic biofortification), and micronutrient fertilisation (i.e. agronomic biofortification). Biofortification is a process of increasing the content or density of a specific micronutrient in food or feed crops. Genetic biofortification uses specially bred crops that have been selected on the basis of their ability to concentrate the specific micronutrient, such as Zn or Fe, in their edible parts, and in a bioavailable form.

Farming for health is a sustainable means of achieving better nutrition and health for people worldwide (Welch, 2005). Increasing the micronutrient content of edible parts of staple food crops, by adopting agricultural practices that are designed to benefit human nutrition, can be done with known technologies, including choice of cropping systems, agronomic practices, variety selection, as well as through the use of modern molecular technologies (Welch, 2001).

Table 10.1. Essential micronutrients for humans, livestock and crops (Welch, 2008; Alloway, 2008c).

	HUMANS	LIVESTOCK	CROPS		HUMANS	LIVESTOCK	CROPS
Boron				Fluorine			–
Cobalt				Iodine			–
Copper				Selenium			–
Iron				Chlorine	–	–	
Manganese				Chromium		–	–
Molybdenum				Silicon		–	–
Zinc							

Agronomic biofortification is aimed at increasing the density and balance of nutrients essential to humans (e.g. Zn, Se, B and I) in harvested crop products, mainly by means of appropriate plant nutrition and crop management practices. Unfortunately, though Fe is as important as Zn to humans, its mobility within the plant is restricted, and foliar or soil applications have very little or no effect on the amount accumulated in edible grain. On the other hand, foliar or combined soil plus foliar applications of Zn fertiliser have been found to be effective in maximising uptake and accumulation of Zn in wheat grain (Cakmak, 2008b; c). In Turkey, a long-term programme on Zn fertilisation has been implemented in the cereal growing area of Central Anatolia to correct the identified deficiency. This programme resulted in very significant yield gains. Many fertiliser producers in Turkey have manufactured NPK fertilisers supplemented with Zn, increasing the use of Zn-enriched NPK fertilisers significantly (see Chapter 7).

Selenium is another important micronutrient for humans and livestock, but it is not yet shown to be essential for plants (Graham *et al.*, 2005). In 1987, the governments of Finland and New Zealand mandated the addition of Se in fertilisers used in the production of feedstuff and food. The target was to increase the Se content of Finnish cereal grains to 0.1mg/kg dry matter and the average Se intake to a safe and adequate range of 0.05-0.20 mg per day (National Research Council, 1980, cited from Hartikainen and Ekholm, 2001). Finland mandated the use of selenate (SeO_4^-) at the rate of 10 g Se/ha in 1998, while New Zealand allowed 1 % Se granulate mixed in bulk blends.

Finland and New Zealand were the first countries to take this step of fertiliser enrichment with an element necessary for animals and humans, but not essential for plant growth. Finland made its decision on food quality grounds, while New Zealand based its need on animal health (Fertilizer International No. 248, April 1987). Broadley *et al.* (2006) reported that agronomic biofortification is also being seen as a strategy to enrich cereal grains with Se in the UK.

Genetic biofortification, or breeding plants with traits that result in significant accumulation of bioavailable micronutrients in the edible portions of staple food, is a more long-term approach to combat malnutrition. It is potentially more cost-effective compared to food fortification or micronutrient supplementation programmes. However, genetic improvement of crops to achieve biofortification is a long-term process and realisation of its potential benefits could be affected by many factors.

HarvestPlus is an interdisciplinary alliance of institutions and scientists working to improve the nutritional status of the poor by biofortifying staple food crops in micronutrients. Initial programmes are on the genetic enhancement of micronutrients in beans, cassava, maize, rice, sweet potatoes and wheat. The programme is also examining the potential for Zn enhancement through agronomic biofortification.

Environmental policies

Environmental policies relating to micronutrients mostly focus on the need to prevent environmental contamination with non-nutritive trace elements associated with some micronutrient sources. In some cases, policies relate to the application of nutritive trace elements as well, since the margin between deficiency and toxicity levels can be relatively narrow for some nutrients.

Non-nutritive trace elements in fertilisers

Some fertilisers, depending on the source, contain or are contaminated with, non-nutritive trace elements. In 1979, Canada established soil-loading limits for phosphate and micronutrient fertilisers that regulated the total amount of nine elements (As, Cd, Co, Hg, Mo, Ni, Pb, Se and Zn) that can be applied in fertilisers over a 45-year period (Table 5.5).

Over 50 years ago, individual states of the USA developed regulations that limited the application of heavy metals in fertilisers. About 10 years ago, a new national programme was established by the Association for American Plant Food Control Officials (AAPFCO) to achieve uniform fertiliser regulations in each state. Current recommendations by AAPFCO (2006) list the maximum allowable concentrations of heavy metals in phosphate and micronutrient fertilisers. The loading is based on the overall rate of application of the plant nutrients in the fertiliser. This subject is discussed further in Chapter 5.

In Australia, regulators have set maximum permissible concentrations of impurities in fertiliser products. For instance, Cd levels should not exceed: 300 mg Cd/kg P in all phosphate fertilisers containing 2 % P or more; 50 mg Cd/kg of product for micronutrient fertilisers; and 10 mg Cd/kg of product for all other fertilisers. The Hg level for all fertiliser types must not exceed 5 mg Hg/kg of product. The Pb concentration of micronutrient fertilisers that are soil-applied shall not be higher than 2000 mg Pb/

kg of product and it shall not exceed 500 mg Pb/kg of product for other application methods of micronutrient fertilisers (FIFA, 2007).

In Brazil, Cd levels in mixed and complex fertilisers supplying macro- and micronutrients with 5 % P_2O_5 or more shall not exceed 57 mg Cd/kg of product. For fertilisers containing less than 5 % P_2O_5, the maximum permissible Cd level is set at 20 mg Cd/kg of product. Zinc and Cu are considered as residues/by-products by the Brazilian Environmental Agency and, as such, they are subject to very restrictive controls. In this regard, the Brazilian fertiliser industry association (ANDA) is working with the Ministry of Agriculture and the Environmental Agency to establish procedures and criteria to reclassify Zn and Cu as products, and not as residues (Normative ruling "SDA" NR 27, 2006).

In India, the heavy metal content of micronutrient fertilisers is restricted. The maximum permissible content is set at 0.003 % maximum by weight of product for Pb, 0.1 % for Cu, 0.0025 % for Cd, and 0.5 % for both Fe and Al (Fertilizer Control Order, 1985).

Use of sewage sludge and industrial by-products as micronutrient sources

The use of sewage sludge and industrial by-products as alternative sources of plant nutrients is a means of recycling wastes. The advantages and disadvantages in the use of sludge should, however, be carefully weighed, and caution has to be taken in their application. Several countries, like Canada and some EU member countries, have acted to regulate the use of industrial by-products as micronutrient fertiliser sources (Westfall *et al.*, 2005).

Application of sludge has been shown to increase the soil content in non-nutritive trace elements or heavy metals such as Cd, Hg and Pb. The use of sludge, encouraged by the US Environmental Protection Agency Policy (USEPA 503 Rule), has raised concerns among some scientists regarding food safety and long-term soil productivity. Current recommendations by AAPFCO (2006) list the maximum allowable concentrations of heavy metals in phosphate and micronutrient fertilisers, but not in sludge, even though sludge contributes to the heavy metal loading of soils. Therefore, it has been agreed in the USA that "any additional regulations concerning fertiliser nutrients and applications should be scientific, based on proper assessment of health risk, and uniformly applied (throughout the USA), and standards must be fertiliser-specific and health risk-based" (Fertilizer International No. 378, Sept/Oct 2000).

Throughout the EU, applying sludge to agricultural land is regulated by Council Directive 86/278, which is enforced by the Sludge (Use in Agriculture) Regulations 1989 with amendments. The regulation prevents people from applying sewage sludge to agricultural lands when the concentrations of certain heavy metals in the soil (Pb, Cd, Hg, Cu, Zn and Ni) are greater than specified limits that vary according to soil pH. Permissible concentrations for the UK are given in Table 10.2.

Soil-applied fertilisers and sewage sludge containing non-nutritive micronutrients can be a concern from an environmental point of view. Thus, foliar sprays with high efficacy, high purity and fully formulated micronutrient products are becoming popular alternatives to soil applications.

Table 10.2. Maximum permissible concentrations of potentially toxic elements (PTEs) in soil after application of sewage sludge to agricultural land, and maximum annual rates of addition in the United Kingdom (MAFF, 1998).

Element	Maximum permissible PTE concentrations in soils (mg/kg of dry solids) Soil pH[1]				Allowable yearly additions over a period of 10 years (kg/ha)[2]
	pH 5.0-5.5	pH 5.5-6.0	pH 6.0-7.0	pH >7.0[3]	
Zinc	200	250	300	450	15
Copper	80	100	135	200	7.5
Nickel	50	60	75	110	3
	For pH 5.0 and above				
Cadmium	3				0.15
Lead	300				15
Mercury	1				0.1
Chromium	400 (p)				15 (p)
Molybdenum	4				0.2
*Selenium	3				0.15
*Arsenic	50				0.7
*Fluoride	500				20

(p) – provisional.
* Not subject to the provisions of the EU Directive 86/278/EEC.
1 For soils in the pH range 5-6, provisional permitted concentrations for Pb, Zn, Cu, Ni and Cd were to be reviewed.
2 Annual rate of application to any site shall be determined by averaging over a 10-year period ending with the year of application.
3 Applies only to soils containing more than 5 % calcium carbonate.

Regulations on micronutrient fertilisers

Nutrients must be made available to the crops when and where needed, at the right rate, and micronutrient application is no exception. However, inadequate information on the benefits of micronutrient use and, sometimes, poor quality micronutrient fertiliser products constrain if not dissuade farmers from purchasing micronutrient fertilisers.

Regulation is a recourse taken by governments to protect the consumers against low-quality products, and safeguard the environment from possible contamination with undesired elements. Quality standards and product registration are the two primary forms of fertiliser regulation or control.

Fertiliser registration and quality standards

Government departments normally handle fertiliser product registration. Any entity wishing to commercialise fertilisers has to submit an application before the product is put in the marketplace. Product details such as nutrient content, formulation, physical and chemical characteristics, among others, must be specified, or should be within the limits set by the regulating authorities. Product registration for most fertilisers, including micronutrients, is practised in most developed countries like France, Germany, Japan, Poland and the USA, and in developing ones such as in Argentina, Brazil, India, Iran, the Philippines and Vietnam.

The Indian Fertiliser Control Order (FCO) of 1985, amended in 2006, regulates the maximum amount of micronutrients added to fertilisers as follows:

- boronated single superphosphate (16 % P_2O_5 powdered): maximum 0.18 % B by weight;
- zincated urea (43 % N minimum): minimum 2.0 % Zn by weight;
- zincated phosphate (suspension): minimum 19.4 % Zn by weight.

In the USA, the uniform state fertiliser bill promulgated by AAPFCO suggests regulations for all plant nutrients. The bill lists the minimum percentages of each micronutrient that could be accepted for registration, and gives allowable tolerances for each micronutrient in relation to the content guaranteed by the manufacturer on the fertiliser label.

The EU directive for fertilisers is aimed at removing barriers to trade, and at creating a single common market among member countries, so that, if a fertiliser product has been approved in one member country, it can be marketed in another without undergoing a different process of registration (EEC Directive 76/116). This directive includes secondary and micronutrients. However, some countries still require compliance to their national legislation. Thus, a two-tier regulation is imposed on the marketing of some fertilisers (Table 10.3).

The Australian (Draft) Code of Practice for Fertiliser Description and Labelling, promulgated by the Fertilizer Industry Federation of Australia (FIFA, 2007), stipulates the minimum levels of allowable inclusion of nutrients on the labels of fertiliser products to prevent misleading claims. Nutrients may only be included on the label if they meet or exceed specified minimum concentrations (Table 10.4).

Quality standards are imposed by some governments to protect consumers and the environment. Standards more often focus on the product composition, labelling and packaging. Parallel to product standards should be the capability of control agencies to verify the product's quality with appropriate analytical methods. The International Standards Organization (ISO) and the European Committee for Standardization (CEN) are organizations responsible for the standardization of analytical methods. A number of countries among the top fertiliser consumers have regulations and standards in place, e.g. Australia, Brazil, Germany, Italy, Iran, Japan, New Zealand, Poland, South Africa, Turkey and the USA. China, the largest fertiliser-consuming and producing country, has no fertiliser regulation yet in place (IFA, 2008).

Table 10.3. Minimum micronutrient content (% by weight of fertilisers) according to the EU Regulation on micronutrients (Reg. 2003/2003).

Element	Solid or fluid mixtures of micronutrients*		EC fertilisers containing primary or secondary nutrients with micronutrients for soil application		EC fertilisers containing primary or secondary nutrients with micronutrients for leaf sprays
	Micronutrients in "exclusively mineral" form	Micronutrients in chelated or complexed form	for crops or grassland	for horticultural uses	
Boron	0.2	0.2	0.01	0.01	0.01
Cobalt	0.02	0.02	0.002	-	0.001
Copper	0.5	0.1	0.01	0.002	0.002
Iron	2.0	0.3	0.5	0.02	0.02
Manganese	0.5	0.1	0.1	0.01	0.01
Molybdenum	0.02	-	0.001	0.001	0.001
Zinc	0.5	0.1	0.01	0.002	0.002

* minimum total micronutrient content in a solid mixture: 5 % by mass of the fertiliser.
minimum total micronutrient content in a fluid mixture: 2 % by mass of the fertiliser.

Table 10.4. Minimum levels for inclusion of nutrients in Australia (FIFA, 2007).

Nutrient	Minimum content in solid fertilisers (%)	Minimum content in fluid fertilisers (%)
Cu, Mn, Zn	0.05	0.005
Fe	0.1	0.005
B	0.02	0.005
Co	0.001	0.001
Mo	0.001	0.0005
Se	0.001	-

Government policies and regulations relating to both agricultural production and fertiliser use mostly emphasize macronutrients. In the current food and nutrition security context, policy makers should also take into consideration policies relating to micronutrient use. Micronutrient applications should be encouraged, where needed, to balance plant nutrition and alleviate deficiencies. At the same time, policies should provide for the continuous monitoring of possible toxicity risks. Policies should address consumer demand for improved and varied products and provide incentives to farmers to produce more nutritious and diverse agricultural products.

11. Conclusions and recommendations

Micronutrients in agriculture, horticulture and forestry need to be considered within broader agendas. In Integrated Plant Nutrition Systems, for example, the aim is to "enhance soil productivity through a balanced use of local and external sources of plant nutrients in a way that maintains or improves soil fertility and is environmentally-friendly (FAO, 1995). This aim applies to micronutrients as well as macronutrients. Some authors (Welch and Graham, 2005) advocate that micronutrients should be viewed in an even broader food systems context. In the food systems context, Best Management Practices (BMPs) would optimise micronutrient supply and availability in the entire food consumption cycle. To translate these aims into more practical measures, Bruulsema *et al.* (2008) propose a global framework for BMPs for fertiliser use. These can be applied to micronutrient use in agriculture, horticulture and forestry. Best Management Practices for fertiliser use, including micronutrients, support cropping systems management objectives of profitability, productivity, sustainability and environmental health.

Micronutrients supplied in optimal forms and amounts and with optimal timing and placement, on soils with an inadequate supply, will generate benefits for producers and consumers, providing other factors are not limiting. The principles governing optimal supply, methods of application and timing of application were discussed in detail in Chapters 5 and 6. Provided these principles are adopted and there is a sound knowledge of inputs and outputs of micronutrients in production systems, negative effects of micronutrients should be negligible or manageable. By considering the benefits of micronutrients in harvested plant products for human nutrition and in forages for animal nutrition, the benefits can be further extended beyond those based on yield alone.

Micronutrient deficiencies continue to limit crop production in many parts of the world (Chapter 4). Even in India and China, where extensive national programmes of research were carried out several decades ago to determine the micronutrient status of the soils, recent investigations show that many crops are deficient in micronutrients. This suggests that either existing research knowledge is not being applied in agricultural production, or that cropping systems have changed and previous practices are no longer adequate to correct micronutrient deficiencies.

In other countries, such as Pakistan, recent research is uncovering extensive areas with low micronutrient status and opportunities for increased crop production from micronutrient application. It is likely that many other developing countries are yet to realise the full extent to which micronutrient deficiencies are limiting current and potential agricultural production. At a time when global grain stocks are at their lowest level for more than two decades, and grain shortages have pushed up prices, there are strong incentives to ensure that widespread deficiencies of micronutrients in agriculture are corrected.

In order to meet the growing global demand for cereal grains, it is estimated that production by 2025 needs to increase by 59 % relative to that in 1995 (Cassman, 2006), after allowing for losses of land to biofuel production and urbanisation. Based on growing populations in the regions where rice is the main staple, it was estimated that total rice production should escalate a further 38 % by 2030 (Surridge, 2004). This provides a challenge for breeders to develop cultivars with higher yield potential, for agronomists to develop packages of technologies that allow realisation of yield potential, and for farmers to apply efficient practices to achieve economic returns for their crops in the face of rising fuel prices, increased cost of fertilisers, greater scrutiny of the environmental impacts of agriculture, and the uncertain effects of climate change. Application of BMPs for micronutrients will surely be part of meeting the challenge of increasing global grain production. Most of the global grain output increases will have to come from larger yields. Grain yield increases will be partly offset by: loss of land due to urbanisation and transport infrastructure; decreases in water allocation to crop production, and the impact of global climate change.

As cropping systems evolve, micronutrient supply-demand relationships change. One of the most profound changes in cropping systems is the progressive increase in yield obtained in many crops over the last several decades. For example, globally, rice yields averaged 4 t/ha in 2004, doubling the yield of 1966 (Cassman, 2006). Similar increases in grain productivity have been recorded for all major cereals and many of the main oilseed crops and pulses. Higher yielding crops require greater nutrient supply, including micronutrients, unless efficient varieties are widely employed to meet crop requirements from soil micronutrient reserves. Even with more efficient varieties, whose release to farmers would require a long-term R&D investment, substantial increases in micronutrient application seems inevitable to prevent micronutrient deficiencies becoming more prevalent over time.

Large opportunities exist through BMPs to increase crop production by applying micronutrients. Best Management Practices need to be tailored to local conditions. The development of BMPs for micronutrients would involve:

- **Identifying other limiting factors and correcting them before or while applying micronutrients.** The prevalence of macronutrient deficiencies in many parts of the world obviously stands as an obstacle to the cost-effective use of micronutrients (Chapter 4).
- **Selecting optimal fertiliser type, rate, method and time of application for effective correction of deficiency.** Local conditions determine the optimal combination of fertiliser type, rate, method and time of application. In addition, there is a substantial body of existing practice with micronutrients (Chapters 5 and 6) that will enable a close approximation of optimal practice without the need for expensive experiments in all locations.
- **Determining residual effects of the micronutrient applications over time, including possible toxicity effects on following crops.** Residual value of applied fertilisers is more important for micronutrients than for most macronutrients. Yield and soil reactions are clearly the major determinants of the residual value of added micronutrient fertilisers. Intensive crop production systems, such as the rice-

wheat rotation, which produce over 12 t of grain/ha/yr, remove comparatively large amounts of micronutrients annually. In the high-yield cropping systems, accurate records of yield over time improve the prospects of correctly estimating when further application of micronutrient fertilisers is necessary to maintain adequate supply. In low-yield cropping systems, soil reactions may have a greater role in determining the frequency of re-application of micronutrients. Regardless of the intensity of the cropping system, substantial removal of straw from fields would further decrease the length of residual micronutrient effects on crop production.

- **Calculating nutrient budgets to identify all sources of micronutrient inputs and outputs to detect declining supply or the accumulation of excess.** Flexible low-cost methods are needed to provide up-to-date estimates of the areas where micronutrient applications are needed for productive agriculture. Simple micronutrient budgeting tools, or audits of inputs and outputs can provide a first approximation of imbalances between inputs and outputs (Chapter 7).
- **Monitoring levels in crops and soils by soil and plant analysis.** In addition to nutrient budgets, an accepted means of verifying micronutrient levels in soils and crops is the use of soil and plant analysis (Mortvedt *et al.*, 1991; Reuter and Robinson, 1997; Peverill *et al.*, 1999).

  Soil analysis is effective for predicting the likely occurrence of most micronutrient deficiencies and to monitor changes in soil status over time (McLaughlin *et al.*, 1999). When used for prediction of a likely deficiency, a soil sample taken before sowing can be analysed to determine what corrective fertiliser application is needed to avoid the deficiency. This use of soil analysis is most helpful to farmers since it allows for a corrective action before yield loss is experienced. However, reliable interpretation of soil analysis depends on adequately calibrated data for the soil test with the crop and soil under investigation. By contrast, plant analysis calibration data is more widely applicable even when established on other soil types.

  Monitoring soil micronutrient levels over a period of time allows land managers to detect trends in micronutrient status and to adjust fertiliser programmes accordingly to avoid either deficiency developing or excess micronutrient accumulating in the soil. However, adoption of soil analysis remains relatively low, even in developed countries. In the USA and Australia, for example, 15 and 10-20 % of the fields, respectively, were reported in the early 1990s to be soil tested (Jones, 1993; Peverill, 1993). In developing countries, the use of soil and plant analysis is even less common for practical fertiliser management on farms. Increases in fertiliser prices may trigger a greater interest in the use of soil and plant analysis to optimise nutrient supply and the economic return.

  The care required to avoid contamination and to obtain reliable micronutrient data from soil and plant analysis greatly exceeds that required with collecting and handling samples for macronutrient analysis. Minute amounts of a contaminant are sufficient to cause erroneous results with micronutrient analysis. Soil and plant analysis need considerable local calibration for most accurate prognosis and, in many parts of the world, this local calibration work is yet to take place.

- **Utilise genotypic efficiency.** For all micronutrients, species vary in their response to low soil levels (Graham, 1991). Hence, there is scope for growing species that have a low micronutrient response in order to minimise the need for fertilisers. More recent research has focussed on differences in efficiency between genotypes to widen the scope for managing micronutrient deficiencies. Efficient genotypes are able to acquire micronutrients from the soil more effectively and achieve higher yields than a standard cultivar (Graham, 1984).

  In practical terms, this means that micronutrient fertiliser could be avoided in some cases, or that lower amounts could be applied when growing an efficient species or cultivar on soils low in micronutrients. In the long term, the wisdom of the strategy depends on the magnitude of the soil micronutrient reserves (Graham, 1984). If the soil reserves are very large in relation to crop demand, and the primary constraint for crops is low micronutrient availability, then increased efficiency is an effective corrective strategy, and it is not likely to lead to the depletion of the soil micronutrient content (Graham and Rengel, 1993). If on the other hand, the micronutrient deficiency is due to very low levels in the soil, then efficiency would be, at best, an interim solution.

  According to Graham and Rengel (1993), breeding for nutrient efficiency in crop species is only likely to be adopted as a solution for micronutrient deficiency if the problem is difficult to solve by conventional agronomic means using fertilisers, and if the area affected is large. Hence, most resources in selecting for efficient genotypes should be focused on the major crops in a region, usually the cereals. However, breeding for nutrient efficiency could be counterproductive if it leads to varieties with greater internal efficiency and not greater uptake efficiency. This would result in lower micronutrient concentrations in grain that might have detrimental health effects.
- **Managing crop nutrition to achieve adequate micronutrient levels in harvested products for human nutrition.**

Emerging cropping systems such as rice-maize rotations and water-saving rice production will require a careful examination of micronutrient supply for productive and sustainable cropping. The shift from paddy to aerobic rice may result in increased Zn fertiliser use. The requirement for other micronutrients may also be affected. Emerging intensive rice-maize cropping systems in Asia are also likely, as with rice-wheat systems, to have high micronutrient demand. Expansion of biofuel crop production will create micronutrient budgeting issues that may affect the productivity of those cropping systems. For example, cassava produced in Thailand is being exported for ethanol production elsewhere, and is depleting soil nutrient reserves.

Organic agriculture is an emerging food production system that has been growing rapidly over the past decade or more. The optimal supply of micronutrients in these production systems has rarely been considered. However, with the spread of organic agriculture, micronutrient supply may attract more attention, especially if linked with the rise in consumer interest in micronutrient levels in food for human nutrition. It is possible that the transition of cropping systems from conventional to organic management practices may initially sequester more micronutrients into soil organic matter and require greater micronutrient inputs until a new equilibrium of biogeochemical cycling occurs.

In the most severely deficient soils, the application of micronutrient fertiliser makes an absolute difference between being able to use land productively for agriculture, horticulture or forestry, or not. In developing countries, some estimates predict the development of 120 million hectares of new cropping land by 2030 (Alexandratos, 2005). The vast majority of this land would be in sub-Saharan Africa and Latin America (Alexandratos, 2005). From experience elsewhere in the world, land managers, extension officers and researchers need to be warned about the possibility of acute micronutrient deficiencies, when and where new land is converted to agriculture. Severe micronutrient deficiencies arose following clearing of primary and secondary forests in many upland areas in Asia. There is little doubt that similar issues will occur elsewhere due to infertile soils or loss of soil fertility.

Examples of severe micronutrient deficiencies following forest clearing include:
- B deficiency after clearing in parts of Sumatra, Mindanao, Laos, Hainan and Yunnan;
- Fe deficiency in western Sumatra and central Thailand;
- Zn deficiency in southern China, and;
- Cu deficiency in Indonesia.

The adoption of new cropping practices may greatly alter the availability of micronutrients to crops. For example, the widespread adoption of zero tillage changes the mixing of micronutrients in soil profiles, and the concomitant use of herbicides may also impact on nutrient uptake efficiency (Chapter 8). In 2003/04, about 90 million ha were under no-till systems, mostly in North America, Brazil, Argentina and Australia (Derpsch and Benites, 2004). No-till is rapidly being adopted in the Indo-Gangetic Plain. In the only study to date investigating vertical distribution of organic matter and micronutrients in relation to no-till and tillage practices, Teixeira *et al.* (2003) showed that no-till reduced the homogeneity of micronutrients in soils, presumably due to the greater concentration of organic matter near the surface. It remains to be determined whether no-till will alter the residual effect of micronutrient fertilisation. However, BMPs for micronutrients in these systems and others need to evolve as the systems evolve.

Emerging spatial data analysis techniques have an application in defining the areas where micronutrient deficiencies are most likely to occur. Weight of evidence modelling, which uses existing data sets commonly found in soil surveys, has promise as a surrogate for costly, extensive soil analysis programmes. Since there is already evidence that soil analysis is not used to its potential, alternative strategies are needed to identify where fertiliser BMPs should include micronutrients.

One of the major challenges to the development and adoption of BMPs is the evidence in many countries that known micronutrient deficiencies are not being treated on farms. It is clear that market failures are occurring in the supply of micronutrients to soil and crops, especially in developing countries. Some of the market failures are due to the inadequate delivery of knowledge about micronutrient deficiencies to farmers. Innovative approaches to communication are needed where government extension services have been ineffective because of inadequate resources or staffing.

Together with improved information to the farmers, and creating a demand for micronutrients, there is a need for a reliable supply of micronutrients in local markets at prices that growers can afford. Micronutrient enrichment of the most-commonly used macronutrient fertilisers is likely to be the easiest mechanism for delivering micronutrients to large numbers of small farmers. Fertiliser importers, manufacturers and distributors play a critical role in developing and supplying appropriate micronutrient-enriched fertilisers to the farmers. Information about micronutrient responses and suitable fertiliser products needs to flow more freely between agriculture, horticulture and forestry enterprises in the same region.

Food production systems need to be more than just producers of carbohydrates. They should also consider the levels and availability to consumers of the other essential nutrients, including micronutrients in food. Presently, over 3 billion people suffer from micronutrient malnutrition. Micronutrient deficiencies explain many deaths of children, and marginal intake of micronutrients in the diet contributes to poor learning ability, and impaired growth and development of children (Chapter 3). Improved nutritional quality of crops can be achieved by agronomic methods as well as breeding strategies. Both strategies can be used to increase the micronutrient density of plant foods, which, in turn, increases intake in the human diet. Existing BMPs for fertiliser use could readily be modified to ensure that micronutrient density in food is improved.

As the market for grain with high levels of bioavailable micronutrients expands, grain producers are likely to seek varieties that can satisfy consumer's demand for micronutrient-dense grain, and to expect to obtain a price premium for supplying such grain into the market. However, such market driven demand is less likely to influence production in developing countries than in the developed countries. In developing countries, an argument can be mounted for treating the micronutrient levels in grains as a public health issue, rather than as an agricultural research issue. If markets fail to deliver signals to the farmers to produce micronutrient-dense grain, while widespread micronutrient malnutrition exists in the population, there is a powerful argument for government interventions to stimulate this development. The subsidised Zn-enriched NPK fertiliser programme of the government of Turkey resulted in a dramatic increase in purchases of Zn-enriched fertilisers (Cakmak, 2008c). While the benefits for public health in Turkey have not been quantified, typical Zn application rates can double the grain Zn content in wheat.

In order to boost micronutrient levels in food, policy can support subsidies for micronutrient–enriched fertilisers (as practised in Turkey), or to mandate micronutrient additions to fertilisers in regions where deficiency is prevalent (as practised with Se additions in Finland), or else allow market signals to operate on supply and demand for such products. The efficacy of the policy will vary from country to country, depending on how well the benefits of subsidies can be targeted and whether they cause counter-productive market distortions in supply or demand. Mandatory additions of micronutrients to fertiliser are only useful as a policy if there is no economic incentive for farmers to use micronutrients. Despite the potential drawbacks with interventions, action is needed to overcome market failure that is evident in the supply of appropriate micronutrients in many developing countries, where crop productivity and human health would greatly benefit from their availability.

Training in micronutrients is needed across all sectors of the fertiliser industry, including those involved in:

- manufacturing fertilisers,
- storing fertilisers,
- handling and distributing fertilisers,
- dealing with customers in a fertiliser sales capacity, and
- providing advice and recommendations for fertiliser use.

The future supply of micronutrients to agriculture and horticulture needs to recognise that it will face increasing public scrutiny of its impacts on food safety and environmental quality. The on-going importance of micronutrients in agriculture requires comprehensive programmes to train human resources in each country. Innovative industry-wide programmes, such as FertCare in Australia, are a useful model for examination.

Clearly, the capacity to mount such training programmes is greater in developed countries than in most developing countries. However, it is important that training is not just restricted to universities, notwithstanding the key role they play in developing capacity for training, advising farmers and conducting research. Possibly, the group that is most often left out of the training process is the fertiliser sales staff in developing countries. Small businesses selling fertiliser to farmers in developing countries occupy a unique position in terms of access to farmers. With better training, these groups could become important channels of information, provided their advice is seen as independent and well-informed. Accreditation programmes for such people may build consumers' confidence in the quality of advice. However, when advice is limited to the product being sold, consumers may be concerned about the partiality of advice provided. There also remains an important role for the government to act as an independent voice in the evaluation and registration of products and in maintaining quality control.

The rapid development of research capacity and outputs in the molecular biology of micronutrients is generating important new understanding of the role of these elements in plants, and the potential to transform plants for improved micronutrient status. However, there remains the need to maintain and develop understanding of the physiology of micronutrients in plants, and of the behaviour of micronutrients in the soil and in biogeochemical cycles in diverse agricultural, horticultural and forest (including plantation forests) systems. This requires an increase in R&D (soil science, plant physiology, etc.) efforts to embrace long-term monitoring, new crops and new practices. Now, such R&D is generally declining, except for molecular/breeding research programmes. The major challenges are to (1) deliver existing knowledge about micronutrients to farmers; (2) overcome market failures in delivery of cost-effective products to growers; and (3) understand the long-term biogeochemical cycling of micronutrients in the farming and food systems. A key pathway for the delivery of knowledge on micronutrients to the grower is through the network that now exists for the supply of N, P and K fertilisers throughout the world.

12. References

AAPFCO (2006). Metals in Fertilizers. p. 62. In *AAPFCO Official Publication No. 59*. Association for American Plant Food Control Officials, West Lafayette, Indiana.

AAPFCO and TFI (2006). *Commercial Fertilizers: A Summary of Fertilizer Use in the United States*. Association of American Plant Food Control Officials (AAPFCO) and The Fertilizer Institute (TFI), Washington, D.C.

Adriano, D.C. (2001). *Trace Elements in Terrestrial Environments. Biogeochemistry, Bioavailability, and Risks of Metals*. 2nd ed. Springer-Verlag, New York.

AFSA/FIFA (2006). *Fertcare Handbook*. Australian Fertiliser Services Association (AFSA) and Fertilizer Industry Federation of Australia (FIFA), Canberra.

Ahmed, M., Jahiruddin, M., Jamjod, S. and Rerkasem, B. (2002). Boron efficiency in wheat germplasm from Bangladesh. p. 299-303. In H.E. Goldbach, B. Rerkasem, M.A. Wimmer, P.H. Brown, M. Thellier and R.W. Bell (eds.), *Boron in Plant and Animal Nutrition*. Kluwer Academic/Plenum Publishers, New York.

Alexandratos, N. (2005). *World Agriculture. Towards 2010*. FAO, Rome & Wiley, Chichester.

Ali, A., Yousaf, C.M. and Tufail, M. (1988). Screening of desi and kabuli chickpea types for iron-deficiency chlorosis. International Chickpea Newsletter 18: 5-6.

Alloway, B.J. (ed.) (1995). *Heavy Metals in Soils*. 2nd ed. Blackie and Son Ltd., London.

Alloway, B.J. (2008a). *Zinc in Soils and Crop Nutrition*. 2nd ed. International Zinc Association (IZA) and International Fertilizer Industry Association (IFA), Brussels and Paris.

Alloway, B.J. (2008b). Micronutrients and crop production: An introduction. p. 1-39. In B.J. Alloway (ed.), *Micronutrient Deficiencies in Global Crop Production*. Springer, Dordrecht.

Alloway, B.J. (ed.) (2008c). *Micronutrient Deficiencies in Global Crop Production*. Springer, Dordrecht.

Alva, A.K. (1993). Copper contamination of sandy soils and effects on young Hamlin orange trees. Bulletin of Environmental Contamination and Toxicology 51: 857-864.

Alvarez, J.M. and Gonzalez, D. (2006). Zinc transformations in neutral soil and zinc efficiency in maize fertilization. Journal of Agricultural and Food Chemistry 54: 9488-9495.

Álvarez-Fernández, A., Garcia-Marco, S. and Lucena, J.J. (2005). Evaluation of synthetic iron(iii)-chelates (EDDHA/Fe^{3+}, EDDHMA/Fe^{3+} and the novel EDDHSA/Fe^{3+}) to correct iron chlorosis. European Journal of Agronomy 22: 119-130.

Andersen, P., Tuladhar, J.K., Karki, K.B. and Maskey, S.L. (2005). *Micronutrients in South and South East Asia*. International Centre for Integrated Mountain Development, Kathmandu.

Anonymous (1998). *Micronutrients in Agriculture: Pakistani Perspective*. p. 51. National Fertilizer Development Center, Islamabad, Pakistan.

Armstrong, T.A. and Spears, J.W. (2001). Effect of dietary boron on growth performance, calcium and phosphorus metabolism, and bone mechanical properties in growing barrows. Journal of Animal Science 79: 3120-3127.

Arnon, D.I. and Stout, P.R. (1939). Molybdenum as an essential element for higher plants. Plant Physiology 14: 599-602.

Ascher-Ellis, J.S., Graham, R.D., Hollamby, G.J., Paull, J., Davies, P., Huang, C., Pallotta, M.A., Howes, N., Khabaz-Saberi, H., Jeffries, S.P. and Moussavi-Nik, M. (2001). Micronutrients. p. 219-240. In M.P. Reynolds, J.I. Ortiz-Monasterio and A. McNab (eds.), *Application of Physiology to Wheat Breeding*. CIMMYT, Mexico, DF.

Asher, C.J. (1991). Beneficial elements, functional nutrients, and possible new essential elements. p. 703-724. In J.J. Mortvedt, F.R. Cox, L.M. Shuman and R.M. Welch (eds.), *Micronutrients in Agriculture*. 2nd ed. SSSA Book Series No. 4. Soil Science Society of America, Madison, Wisconsin.

Auza, N., Olson, W.G., Tapia, O. and Murphy, M.J. (2002). A review of the role of molybdenum in animal nutritional physiology and pathophysiologic aspects. Journal of Animal and Veterinary Advances 1: 104-109.

Bai, C., Reilly, C.C. and Wood, B.J. (2006). Nickel deficiency disrupts metabolism of ureides, amino acids, and organic acids of young pecan foliage. Plant Physiology 140: 433-443.

Baik, H.W. and Russell, R.M. (1999). Vitamin B12 deficiency in the elderly. Annual Review of Nutrition 19: 357-377.

Baker, A.S. and Mortensen, W.P. (1966). Residual effect of single borate application on western Washington soils. Soil Science 102: 173-179.

Baker, D.E. and Senft, J.P. (1995). Copper. p. 179-205. In B.J. Alloway (ed.), *Heavy Metals in Soils*. 2nd ed. Blackie Academic and Professional, London.

Bandyopadhyay, S., Bhattacharya, I., Ghosh, K. and Varadachari, C. (2008). New slow-releasing molybdenum fertilizer. Journal of Agricultural and Food Chemistry 56: 1343-1349.

Barrett, K.A. and McBride, W.B. (2006). Trace element mobilization in soils by glyphosate. Soil Science Society of America Journal 70: 1882-1888.

Barrow, N.J. (1987). *Reactions with Variable-Charge Soils*. Martinus Nijhoff Publishers, Dordrecht.

Barrow, N.J. (1989). Testing a mechanistic model. X. The effect of pH and electrolyte concentration on borate sorption by a soil. Journal of Soil Science 40: 427-435.

Barrow, N.J. (1993). Mechanisms of reactions of zinc with soil and soil components. p. 15-32. In A.D. Robson (ed.), *Zinc in Soils and Plants*. Kluwer Academic Press, Dordrecht.

Barton, L.L. and Abadia, J. (2006). *Iron Nutrition in Plants and Rhizospheric Microorganisms*. Springer, Dordrecht.

Bar-Yosef, B. (1999). Advances in fertigation. Advances in Agronomy 65: 1-75.

Beard, J.L. and Connor, J.R. (2003). Iron status and neural functioning. Annual Review of Nutrition 23: 41-58.

Bell, R.W. (1997). Diagnosis and prediction of boron deficiency for plant production. Plant and Soil 193: 149-168.

Bell, R.W. (1999). Boron. p. 309-317. In K. Peverill, L. Sparrow and D.J. Reuter (eds.), *Soil Analysis An Interpretation Manual*. CSIRO Publishing, Melbourne.

Bell, R.W. (2000). Temporary nutrient deficiency - a difficult case for diagnosis and prognosis by plant analysis. Communications in Soil Science and Plant Analysis 31: 1847-1861.

Bell, R.W., Dell, B. and Huang, L. (2002). Boron requirements of plants. p. 63-85. In H.E. Goldbach, B. Rerkasem, M. Wimmer, P.H. Brown, M. Thellier and R.W. Bell (eds.), *Boron in Plant and Animal Nutrition*. Kluwer Academic/Plenum Publishers, New York.

Bell, R.W., Dell, B. and Huang, L. (2004). Importance of micronutrients in crop production. In IFA Symposium on Micronutrients, Dehli, 23-25 February 2004, International Fertilizer Industry Association (IFA), Paris.

Bell, R.W., McLay, L., Plaskett, D. and Loneragan, J.F. (1989). Germination and vigour of black gram (*Vigna mungo* (L.) Hepper) seed from plants with and without boron. Australian Journal of Agricultural Research 40: 273-279.

Bell, R.W., Kirk, G., Plaskett, D., and Loneragan J.F. (1990a). Diagnosis of zinc deficiency in peanut (*Arachis hypogaea* L.) by plant analysis. Communications in Soil Science and Plant Analysis 21: 273-285.

Bell, R.W., Rerkasem, B., Keerati-Kasikorn, P., Phetchawee, S., Hiranburana, N., Ratanarat, S., Pongsakul, P. and Loneragan, J.F. (1990b). *Mineral Nutrition of Food Legumes in Thailand with particular reference to micronutrients.* ACIAR Technical Report. 19. Australian Centre for International Agricultural Research, Canberra.

Beltram, V. (1958). Das Spurelement Bor. (in German). Allgemeine Forstzeitshrift 25/26, 323.

Bennett, W.F. (ed.) (1993). N*utrient Deficiencies and Toxicities in Crop Plants*. APS Press, St Paul, Minnesota.

Berger, K.C. and Truog, E. (1939). Boron determination in soils and plants using quinalizarin reaction. Industrial and Engineering Chemistry, Analytical Edition 11: 540-545.

Bergmann, W. (1992). *Colour Atlas. Nutritional Disorders of Plants: Development, Visual and Analytical Diagnosis*. Gustav Fischer, Verlag Jena, Stuttgart.

Bernards, M.L., Thelen, K.D. and Penner, D. (2005). Glyphosate efficacy is antagonized by manganese. Weed Technology 19: 27-34.

Blamey, F.P.C., Mould, D. and Chapman, J. (1979). Critical boron concentrations in plant tissues of two sunflower cultivars. Agronomy Journal 71: 243-247.

Bosch, R. and Imperial, J. (2000). Biosynthesis of the nitrogenase iron-molybdenum cofactor. Recent Research Developments in Microbiology 4: 131-144.

Braekke, F.H. (1979). Boron deficiency in forest plantations on peatland in Norway. Reports of the Norwegian Forest Research Institute 35: 217-236.

Braun, H.J. (1999). Prospects of Turkey's wheat industry, Breeding and Biotechnology. p. 1-744. In H. Ekiz (ed.), *Hububat Sempozyum*. International Winter Cereal Research Center-Konya.

Brennan, R.F. (1992a). The effect of zinc fertilizer on take-all and the grain yield of wheat grown on zinc-deficient soils of the Esperance region, Western Australia. Fertilizer Research 31: 215-219.

Brennan, R.F. (1992b). The relationship between critical concentration of DTPA extractable zinc from the soil for wheat production and properties of southwestern Australian soils responsive to applied zinc. Communications in Soil Science and Plant Analysis 23: 747-759.

Brennan, R.F. (1994). The residual effectiveness of previously applied copper fertilizer for grain yield of wheat grown on soils of south-west Australia. Fertilizer Research 39: 11-18.

Brennan, R.F. (1996). Availability of previous and current applications of zinc fertiliser using single superphosphate for the grain production of wheat on soils of south western Australia. Journal of Plant Nutrition 19: 1099-1115.

Brennan, R.F. (1999a). Lupin grain yields and fertiliser effectiveness are increased by banding manganese below the seed. Australian Journal of Experimental Agriculture 39: 595-603.

Brennan, R.F. (1999b). Zinc. p. 263-280. In K.I. Peverill, L.A. Sparrow and D.J. Reuter (eds.), *Soil Analysis An Interpretation Manual*. CSIRO Publishing, Collingwood.

Brennan, R.F. (2001). Residual value of zinc fertiliser for production of wheat. Australian Journal of Experimental Agriculture 41: 541-547.

Brennan, R.F. (2005). Zinc application and its availability to plants. PhD Thesis, Murdoch University.

Brennan, R.F. (2006). Long-term residual value of copper fertilizer for production of wheat grain. Australian Journal of Experimental Agriculture 46: 77-83.

Brennan, R.F. and Best, E. (1999). Copper. p. 263-280. In K.I. Peverill, L.A. Sparrow and D.J. Reuter (eds.), *Soil Analysis An Interpretation Manual*. CSIRO Publishing, Collingwood.

Brennan, R.F. and Gartrell, J.W. (1990). Reactions of zinc with soil affecting its availability to clover. I. The relationship between critical concentrations of extractable zinc and properties of Australian soils responsive to applied zinc. Australian Journal of Soil Research 28: 293-302.

Brennan, R.F. and McGrath, J.F. (1988). The vertical movement of zinc on sandy soils in southern Western Australia. Australian Journal of Soil Research 26: 211-216.

Brennan, R.F., Armour, J.D. and Reuter, D.J. (1993). Diagnosis of zinc deficiency. p. 167-181. In A.D. Robson (ed.), *Zinc in Soils and Plants*. Kluwer Academic Publishers, Dordrecht.

Broadley, M.R., White, P.J., Bryson, R.J., Meacham, M.C., Bowen, H.C., Johnson, S.E., Hawkesford, M.J., McGrath, S.P., Zhao, F-J., Breward, N., Harriman, M. and Tucker, M. (2006). Biofortification of UK food crops with selenium. Proceedings of the Nutrition Society 65: 169-181.

Brown, P.H. (2008). Micronutrient use in agriculture in the United States of America: Current practices, trends and constraints. p. 267-286. In B.J. Alloway (ed.), *Micronutrient Deficiencies in Global Crop Production*. Springer, Dordrecht.

Brown, P.H., Welch, R.M. and Cary, E.E. (1987). Nickel: A micronutrient essential for higher plants. Plant Physiology 85: 801-803.

Brownell, P.F. (1979). Sodium as an essential micronutrient element for plants and its possible roles in metabolism. Advances in Botanical Research 7: 118-224.

Broyer, T.C., Charlton, A.B., Johnson, C.M. and Stout, P.R. (1954). Chlorine: a micronutrient element for higher plants. Plant Physiology 29: 526-532.

Bruulsema, T., Witt, C., Garcia, F., Li, S., Rao, T.N., Chen, F. and Ivanova, S. (2008). A global framework for fertilizer BMPs. Better Crops 92: 13-15.

Cakmak, I. (2000). Possible roles of zinc in protecting plant cells from damage by reactive oxygen species. New Phytologist 146: 185-205.

Cakmak, I. (2004). Identification and correction of widespread zinc deficiency in Turkey – a success story (a NATO-Science for Stability project). Proceedings of the International Fertilizer Society 552: 1-26.

Cakmak, I. (ed.) (2008a). Zinc crops 2007: Improving crop production and human health. Plant and Soil 306: 1-116.

Cakmak, I. (2008b). Marschner Review. Enrichment of cereal grains with zinc: Agronomic or genetic biofortification? Plant and Soil 302: 1-17.

Cakmak, I. (2008c). Zinc deficiency in wheat in Turkey. p. 181-200. In B.J. Alloway (ed.), *Micronutrient Deficiencies in Global Crop Production*. Springer, Dordrecht.

Cakmak, I. and Marschner, H. (1988). Increase in membrane permeability and exudation in roots of zinc deficient plants. Journal of Plant Physiology 132: 356-361.

Cakmak, I. and Römheld, V. (1997). Boron deficiency-induced impairments of cellular functions in plants. Plant and Soil 193: 71-84.

Cakmak, I., Kutz, H. and Marschner, H. (1995). Short-term effects of boron, germanium and high light intensity on membrane permeability in boron deficient leaves of sunflower. Physiology Plantarum 95: 11-18.

California Plant Health Association (2002). *Western Fertilizer Handbook*. Interstate Publishers, Danville.

Cara, F.A., Sánchez, E., Ruiz, J.M. and Romero, L. (2002). Is phenol oxidation responsible for the short-term effects of boron deficiency on plasma-membrane permeability and function in squash roots? Plant Physiology and Biochemistry 40: 853-858.

Cassman, K.G. (2006). Ecological intensification of agriculture and implications for improved water and nutrient management. In *International Symposium on Fertigation*, Sept 20-24, Beijing, China.

Chatterjee, C. and Nautiyal, N. (2001). Molybdenum stress affects viability and vigour of wheat seeds. Journal of Plant Nutrition 24: 1377-1386.

Christensen, L.P. (2004). Foliar fertilization in vine mineral nutrient management programs. p. 83-90. In L.P. Christensen and D.R. Smart (eds.), *Proceedings of the Soil Environment and Vine Mineral Nutrition Symposium*. American Society for Enology and Viticulture, June 29-30.

Combs, Jr, G.F. and Gray, W.P. (1998). Chemopreventive agents: selenium. Pharmacology and Therapeutics 79: 179-192.

Crabtree, W.L. (1999). Deep placement of Mn fertiliser on a sandy soil increased grain yield and reduced split seed in *Lupinus angustifolius*. Plant and Soil 214: 9-14.

Crosbie, J., Longnecker, N. and Robson, A.D. (1994). Seed manganese affects the early growth of lupins in manganese-deficient conditions. Australian Journal of Agricultural Research 45: 1469-1482.

Crosbie, J., Longnecker, N., Davies, F. and Robson, A.D. (1993). Effects of seed manganese concentration on lupin emergence. Plant and Soil 155/156: 449-452.

Datnoff, L.E., Snyder, G.H. and Korndorfer, G.H. (eds.) (2001). *Silicon in Agriculture*. Elsevier Press, Amsterdam.

Datta, S. P., Bhadoriaand, P.B.S. and Kar, S. (1998). Availability of extractable boron in some acid soils, West Bengal, India. Communications in Soil Science and Plant Analysis 29: 2285-2306.

Delas, J. (1963). The toxicity of copper accumulated in soils. Agrochimica 7: 258-288.

Dell, B. and Huang, L. (1997). Physiological response of plants to low boron. Plant and Soil 193: 103-120.

Dell, B., Bell, R.W. and Huang, L. (2006). Importance of micronutrients in sustaining crop nutrition. In *Optimizing Resource use Efficiency for Sustainable Intensification of Agriculture*. IFA Agriculture Conference, 27 February to 2 March 2006, Kunming, PR China.

Dell, B., Brown, P.H. and Bell, R.W. (eds.) (1997). *Boron in Soils and Plants: Reviews*. Developments in Plant and Soil Sciences Vol. 77. Kluwer Academic Publishers, Dordrecht.

Dell, B., Huang, L. and Bell, R.W. (2002). Boron in plant reproduction. p. 103-118. In H.E. Goldbach, B. Rerkasem, M. Wimmer, P.H. Brown, M. Thellier and R.W. Bell (eds.), *Boron in Plant and Animal Nutrition*. Kluwer Academic/Plenum Publishers, New York.

Dell, B., Malajczuk, N., Xu, D. and Grove, T.S. (2001). *Nutrient Disorders in Plantation Eucalypts*. 2nd ed. ACIAR Monograph No 74. Australian Centre for International Agricultural Research, Canberra.

Dell, B., Xu, D., Rogers, C. and Huang, L. (2003). Micronutrient disorders in eucalypt plantations: causes, symptoms, identification, impact and management. p. 241-252. In R.P. Wei and D. Xu (eds.), *Eucalyptus Plantations - Research, Management and Development*. World Scientific Publishing Co., Singapore.

Demeyer, A., Verloo, M., Ceustermans, N. and Benoit, F. (2001). Use of lignosulfonates as Fe-chelates for the growth of butterhead lettuce in nutrient film technique (NFT). Acta Horticulturae 548: 125-132.

Derpsch, R. and Benites, J.R. (2004). Agricultura conservacionista no munda. Paper presented at the Brazilian Soil Science Conference, July 2004, Santa Maria, Brazil.

Devirian, T.A. and Volpe, S.L. (2003). The physiological effects of dietary boron. Critical Reviews in Food Science and Nutrition 43: 219-231.

Dixon, G.R. (1996). Repression of the morphogenesis of *Plasmodiophora brassicae* Wor. by boron - a review. In J.S. Dias, D.I. Crute and A.A. Monteiro (eds.), *Proceedings of the International Symposium on Brassicas Ninth Crucifer Genetics Workshop*. Acta Horticulturae 407: 393-401.

Dobermann, A. and Fairhurst, T. (2000). *Rice: Nutritional Disorders and Nutrient Management*. Potash and Phosphate Institute and Potash & Phosphate Institute of

Canada (PPI/PPIC) and International Rice Research Institute (IRRI), Singapore and Makati City, The Philippines.

Donald, C.N. and Prescott, J.A. (1975). Trace elements in Australian crop and pasture production, 1924-1974. p. 7-37. In D.J.D. Nicholas and A.R. Egan (eds.), *Trace Elements in the Soil-Plant-Animal Continuum*. Academic Press, New York.

Duxbury, J.M., Bodruzzaman, M.D., Johnson, S., Mayer, A.B.M., Lauren, J.G., Meisner, C.A. and Welch, R.M. (2005). Impacts of increased mineral micronutrient content of rice and wheat seed/grain on crop productivity and human nutrition in Bangladesh. p. 30-31. In C.J. Li, F.S. Zhang, A. Dobermann, P. Hinsinger, H. Lambers, X.L. Li, P. Marschner, L. Maene, S. McGrath, O. Oenema, S.B. Peng, Z. Rengel, Q.R. Shen, R. Welch, N. Von Wiren, X.L. Yan and Y.G. Zhu (eds.), *Plant Nutrition for Food Security, Human Health and Environmental Protection*. Tsinghua University Press, Beijing.

Eker, S., Ozturk, L., Yazici, A., Erenoglu, B., Römheld, V. and Cakmak, I. (2006). Foliar applied glyphosate substantially reduced uptake and transport of iron and manganese in sunflower (*Helianthus annuus L.*) plants. Journal of Agricultural and Food Chemistry 54: 10019-10025.

Epstein, E. and Bloom, A. (2005). *Mineral Nutrition of Plants: Principles and Perspectives*. 2nd ed. Sinauer Associates, Sunderland, Maryland.

Eswaran, H., Almaraz, R., van den Berg, E. and Reich, P. (1997). An assessment of the soil resources of Africa in relation to productivity. Geoderma 77: 1-18.

EVM (2002). *Review of Iron – Revised Edition*. Expert Group on Vitamins and Minerals EVM/00/12.revisedaug (2002).

Fageria, N.K. (2008). *The Use of Nutrients in Crop Plants*. CRC Press, Boca Raton.

Fageria, N.K. and Stone L.F. (2008). Micronutrient deficiency problems in South America. p. 245-266. In B.J. Alloway (ed.), *Micronutrient Deficiencies in Global Crop Production*. Springer, Dordrecht.

Fageria, N.K., Baligar, V.C. and Clark, R.B. (2002). Micronutrients in crop production. Advances in Agronomy 77: 185-268.

FAO (1995). *Integrated Plant Nutrition Systems*. R. Dudal and R. N. Roy (eds.), FAO Fertilizer and Plant Nutrition Bulletin No. 12, Rome, FAO.

FAO/WHO (2005). *Vitamin and Mineral Requirements in Human Nutrition*, 2nd ed. Geneva, World Health Organization.

Fernández, V. and Ebert, G. (2005). Foliar iron fertilization: A critical review. Journal of Plant Nutrition 28: 2113-2124.

FIFA (2007). *Draft Code of Practice for Fertilizer Description and Labelling*. Fertilizer Industry Federation of Australia (FIFA), Canberra.

Fleming, G.A. (1980). Essential micronutrients. I. Boron and molybdenum. p. 155-176. In B.E. Davies (ed.), *Applied Soil Trace Elements*. John Wiley & Sons, New York.

Flores, H.R., Mattenella, L.E. and Kwok, L.H. (2006). Slow release boron micronutrients from pelletized borates of the northwest of Argentina. Minerals Engineering 19: 364-367.

Follett, R.H. and Lindsay, W.L. (1988). Profile distribution of zinc, iron, manganese, and copper in Colorado soils. Colorado State University, Technical Bulletin LTB88-5. reprint of Tech. Bulletin 110 published in 1970.

Gangloff, W.J., Westfall, D.G., Peterson, G.A. and Mortvedt, J.J. (2002). Relative availability coefficients of organic and inorganic Zn fertilizers. Journal of Plant Nutrition 25: 259-273.

Gao, X., Zou, C., Fan, X., Zhang, F. and Hoffland, E. (2006). From flooded to aerobic conditions in rice cultivation: consequences for zinc uptake. Plant and Soil 280: 41-47.

Gartrell, J.W. (1981). Distribution and correction of copper deficiency in crops and pastures. p. 313-349. In J.F. Loneragan, A.D. Robson and R.D. Graham (eds.), *Copper in Soils and Plants*. Academic Press, Sydney.

Gault, R.R. and Brockwell, J. (1980). Studies of seed pelleting as an aid to legume inoculation. 5. Effects of incorporation of molybdenum compounds in the seed pellet on inoculant survival, seedling nodulation and plant growth of lucerne and subterranean clover. Australian Journal of Experimental Agriculture and Animal Husbandry 20: 63-71.

Gibson, R.S. (2006). Zinc: the missing link in combating micronutrient malnutrition in developing countries. Proceedings of the Nutrition Society 65: 51-60.

Gilkes, R.J. and McKenzie, R.M. (1988). Geochemistry and mineralogy of manganese in soils. p. 23-35. In R.D. Graham, R.J. Hannam and N.C. Uren (eds.), *Manganese in Soils and Plants*. Kluwer Academic Publishers, Dordrecht, The Netherlands.

Gillman, G. and Noble, A. (2005). Environmentally manageable fertilizers: A new approach. Environmental Quality Management 15 (2): 59-70.

Gilmour, J.T. (1977). Micronutrient status of the rice plant. I. Plant soil solution concentrations as a function of time. Plant and Soil 46: 549-557.

Godsey, C.B., Schmidt, J.P., Schlegel, A.J., Taylor, R.K., Thompson, C.R. and Gehl, R.J. (2003). Correcting iron deficiency in corn with seed row-applied iron sulfate. Agronomy Journal 95: 160-166.

Goh, K.J., Gan, H.H., Kew, K.K., Chew, P.S. and Teoh, K.C. (2007). Boron requirement and distribution in the oil palm (*Elaeis guineensis* Jacq.) and some implications on manuring practices. p. 189-204. In F. Xu, H.E. Goldbach, P.H. Brown, R.W. Bell, T. Fujiwara, C.D. Hunt, S. Goldberg and L. Shi (eds.), *Advances in Plant and Animal Boron Nutrition*. Springer, Dordrecht.

Goldbach, H.E., Rerkasem, B., Wimmer, M.A., Brown, P.H., Thellier, M. and Bell, R.W. (eds.) (2002). *Boron in Plant and Animal Nutrition*. Kluwer Academic Publishers, Dordrecht.

Goldberg, S. (1997). Reactions of boron with soils. Plant and Soil 193: 35-48.

Graham, R.D. (1981). Absorption of copper by plant roots. p. 141-163. In J.F. Loneragan, A.D. Robson and R.D. Graham (eds.), *Copper in Soils and Plants*. Academic Press, New York.

Graham, R.D. (1984). Breeding for nutritional characteristics. Advances in Plant Nutrition 1: 57-102.

Graham, R.D. (1988). Genotypic differences in tolerance to manganese deficiency. p. 261-276. In R.D. Graham, R.J. Hannam and N.C. Uren (eds.), *Manganese in Soils and Plants*. Kluwer Academic Publishers, Dordrecht.

Graham, R.D. (1991). Breeding wheats for tolerance to micronutrient deficient soil: present status and priorities. p. 315-332. In D.A. Saunders (ed.), *Wheat for Non-Traditional Warm Areas*. CIMMYT, Mexico DF.

Graham, R. D. (2008). Micronutrient deficiencies in crops and their global significance. p. 41-61. In B.G. Alloway (ed.), *Micronutrient Deficiencies in Global Crop Production*. Springer, Dordrecht.

Graham, R.D. and Ascher, J.S. (1993). Nutritional limitations of subsoils. p. 739-742. In N.J. Barrow (ed.), *Plant Nutrition- from Genetic Engineering to Field Practice*. Kluwer Academic Publishers, Dordrecht.

Graham, R.D. and Rengel, Z. (1993). Genotypic variation in zinc uptake and utilization by plants. p. 107-118. In A.D. Robson (ed.), *Zinc in Soils and Plants*. Kluwer Academic Publishers, Dordrecht.

Graham, R.D. and Stangoulis, J.R.C. (2005). Molybdenum and disease. In L. Dantoff, W. Elmer and D. Huber (eds.), *Mineral Nutrition and Plant Diseases*. APS Press, St Paul, Minnesota.

Graham, R.D. and Webb, M.J. (1991). Micronutrients and disease resistance and tolerance in plants. p. 329-370. In J.J. Mortvedt, F.R. Cox, L.M. Shuman and R.M. Welch (eds.), *Micronutrients in Agriculture*. 2nd ed. SSSA Book Series No. 4. Soil Science Society of America, Madison, Wisconsin.

Graham, R.D., Davies, W.J. and Ascher, J.S. (1985). The critical concentration of manganese in field-grown wheat. Australian Journal of Agricultural Research 36: 145-155.

Graham, R.D., Hannam, R.J. and Uren, N.C. (eds.) (1988). *Manganese in Soils and Plants*. Kluwer Academic Publishers, Dordrecht.

Graham, R.D., Stangoulis, J.C.R., Genc, Y. and Lyons, G.H. (2005). Selenium can increase growth and fertility in vascular plants. p. 208-209. In C.J. Li, F.S. Zhang, A. Dobermann, P. Hinsinger, H. Lambers, X.L. Li, P. Marschner, L. Maene, S. McGrath, O. Oenema, S.B. Peng, Z. Rengel, Q.R. Shen, R. Welch, N. Von Wiren, X.L. Yan and Y.G. Zhu (eds.), *Plant Nutrition for Food Security, Human Health and Environmental Protection*. Proceedings of the XVth International Plant Nutrition Colloquium, 9-13 September 2005, Beijing, China. Tsinghua University Press, Beijing.

Grewal, H.S. and Graham, R.D. (1997). Seed zinc content influences early vegetative growth and zinc uptake in oilseed rape (*Brassica napus* and *Brassica juncea*) genotypes on zinc-deficient soil. Plant and Soil 192: 191-197.

Grewal, H.S., Lu, Z. and Graham, R.D. (1997). Influence of subsoil zinc on dry matter production, seed yield and distribution of zinc in oilseed rape genotypes differing in zinc efficiency. Plant and Soil 92: 181-189.

Grundon, N.J. (1991). Copper deficiency of wheat: effects of soil water content and fertilizer placement on plant growth. Journal of Plant Nutrition 14: 499-509.

Grundon, N.J., Robson, A.D., Lambert, M.J. and Snowball, K. (1997). Nutrient deficiency and toxicity symptoms. p. 37-51. In D.J. Reuter and J.B. Robinson (eds.), *Plant Analysis an Interpretation Manual*. CSIRO Publishing, Collingwood.

Gupta, U.C. (ed.) (1993). *Boron and its Role in Crop Production*. CRC Press, Boca Raton, Florida.

Gupta, U.C. (ed.) (1997a). *Molybdenum in Agriculture*. Cambridge University Press, Cambridge.
Gupta, U.C. (1997b). Soil and plant factors affecting molybdenum uptake by plants. p. 71-91. In U.C. Gupta (ed.), *Molybdenum in Agriculture*. Cambridge University Press, Cambridge.
Gupta, U.C. and Cutcliffe, J.A. (1972). Effects of lime and boron on brown heart, leaf tissue calcium/boron ratios, and boron concentrations of rutabaga. Proceedings of the Soil Science Society of America 36: 936-939.
Gupta, U.C. and Cutcliffe, J.A. (1973). Boron nutrition of broccoli, brussel sprouts, and cauliflower grown on Prince Edward Island soils. Canadian Journal of Soil Science 53: 275-279.
Gupta, U.C. and Cutcliffe, J.A. (1975). Boron deficiency in cole crops under field and glasshouse conditions. Communications in Soil Science and Plant Analysis 6: 181-188.
Gupta, U.C., James, Y.W., Campbell, C.A., Leyshon, A.J. and Nicholaichuk, W. (1985). Boron toxicity and deficiency: a review. Canadian Journal of Soil Science 65: 381-409.
Gupta, V.K. and Mehla, D.S. (1993). Depletion of micronutrients from soil and their uptake in rice-wheat rotation. Journal of the Indian Society of Soil Science 4: 704-706.
Hambidge, M. (2000). Human zinc deficiency. Journal of Nutrition 130: 1344S-1349S.
Hannam, R.J. and Ohki, K. (1988). Detection of manganese deficiency and toxicity in plants. p. 243-259. In R.D. Graham, R.J. Hannam and N.C. Uren (eds.), *Manganese in Soils and Plants*. Kluwer Academic Publishers, Dordrecht.
Harkness, R.W. (1959). Boron deficiency and alternate bearing in avocados. Proceedings Florida State Horticultural Society 72: 311-317.
Harris, D., Rashid, D., Miraj, G., Arif, M. and Shah, H. (2007). 'On-farm' seed priming with zinc sulphate solution – A cost-effective way to increase the maize yields of resource-poor farmers. Field Crops Research 102: 119-127.
Harris, H.C., Parker, M.B. and Johnson, B.J. (1965). Influence of molybdenum content of soybean seed and other factors associated with seed source on progeny response to applied Mo. Agronomy Journal 57: 397-399.
Harter, R.D. (1991). Micronutrient adsorption-desorption reactions in soils. p. 59-87. In J.J. Mortvedt, F.R. Cox, L.M. Shuman and R.M. Welch (eds.), *Micronutrients in Agriculture*. 2nd ed. SSSA Book Series No. 4. Soil Science Society of America, Madison, Wisconsin.
Hartikainen, H. (2005). Biogeochemistry of selenium and its impact on food chain quality and human health. Journal of Trace Elements in Medicine and Biology 18: 309-318.
Hartikainen, H. and Ekholm, P. (2001). Selenium inclusion in fertilisers to correct an inadequate national dietary intake. The International Fertilizer Society, Proceeding 467.
Hashim, M.Y. (1984). Potential and problem of peat for agriculture in Malaysia. p. 3-10. In E. Pushparajah and C.B. Wong (eds.), P*roceedings of the Workshop on*

Classification and Management of Peat in Malaysia. Malaysian Society of Soil Science, Kuala Lumpur, Malaysia.

Hazen, J.L. (2000). Adjuvants – terminology, classification, and chemistry. Weed Technology 14: 773-784.

He, Z.L., Yang, X.E. and Stofella, P.J. (2005). Trace elements in agroecosystems and impacts on the environment. Journal of Trace Elements in Medicine and Biology 19: 125-140.

He, Z.L., Zhang, M., Yang, X.E. and Stofella, P.J. (2006). Release behaviour of copper and zinc from sandy soils. Soil Science Society of America Journal 70: 1699-1707.

Hignett, T.P. and McClellan, G.H. (1985). Sources and production of micronutrient fertilizers. Developments in Plant Soil Sciences 14: 237-260.

Hille, R. (1999). Molybdenum enzymes. Essays in Biochemistry 34: 125-137.

Ho, E. (2004). Zinc deficiency, DNA damage and cancer risk. The Journal of Nutritional Biochemistry 15: 572-578.

Hobbs, J.A. and Bertramson, B.R. (1949). Boron uptake by plants as influenced by soil moisture. Soil Science Society of America Proceedings 13: 257-261.

Hodgson, J.F., Lindsay, W.F. and Trierweiler, J.F. (1966). Micronutrient cation complexation in soil solution. II. Complexing of zinc and copper displaced from calcareous soils. Soil Science Society of America Proceedings 30: 723-726.

Holloway, R.E., Bertrand, I., Frischke, A.J., Brace, D.M., McLaughlin, M.J. and Shepperd, W. (2001). Improving fertiliser efficiency on calcareous and alkaline soils with fluid sources of P, N and Zn. Plant and Soil 236: 209-219.

Holloway, R.E., Graham, R.D. and Stacey, S.P. (2008). Micronutrient deficiencies in Australian field crops. p. 63-92. In B.G. Alloway (ed.), *Micronutrient Deficiencies in Global Crop Production*. Springer, Dordrecht.

Hotz, C. and Brown, K.H. (eds.) (2004). Assessment of the risk of zinc deficiency in populations and options for its control. International Zinc Nutrition Consultative Group. Food and Nutrition Bulletin 25: S91-S204.

Hou, J., Evans, L.T. and Speiers, G.A. (1996). Chemical fractionation of soil boron: I. Method development. Canadian Journal of Soil Science 76: 485-491.

Howeler, R.H., Flor, C.A. and Gonzalez, C.A. (1978). Diagnosis and correction of B deficiency in beans and mungbeans in a Mollisol from Cauca valley of Columbia. Agronomy Journal 70: 493-497.

Huang, L., Gherardi, M., Bell, R.W. and Dell, B. (2002). High light intensity increases external B requirements for leaf growth of sunflower (*Helianthus annuus* L. cv. Hysun 25) in boron-buffered (B) solution culture. p. 213-225. In H.E. Goldbach, B. Rerkasem, M.A. Wimmer, P.H. Brown, M. Thellier and R.W. Bell. (eds.), *Boron in Plant and Animal Nutrition*. Kluwer Academic Publishers, Dordrecht.

Huang, L., Ye, Z., Bell, R.W. and Dell, B. (2005). Boron nutrition and chilling tolerance of warm climate crop species. Annals of Botany 96: 755-767.

Huang, L.B., Pant, J., Bell, R.W., Dell, B. and Deane, K. (1996). Effects of boron deficiency and low temperature on wheat sterility. p. 90-102. In H.M. Rawson and K.D. Subedi (eds.), *Sterility in Wheat in Subtropical Asia: Extent, Causes and Solutions*. ACIAR

Proceedings No. 72. Australian Centre for International Agricultural Research, Canberra.

Huett, D.O. and Gogel, B.J. (2000). Longevities and nitrogen, phosphorus, and potassium release patterns of polymer-coated controlled-release fertilizers at 30°C and 40°C. Communications in Soil Science and Plant Analysis 31: 959-973.

Hulthen, L. (2003). Iron deficiency and cognition. Scandinavian Journal of Nutrition 47: 152-156.

Hunt, C.D. (2003). Dietary boron: An overview of the evidence for its role in immune function. Journal of Trace Elements in Experimental Medicine 16: 291-306.

IFA (2008). Micronutrient Fertilizer Use Survey Results. International Fertilizer Industry Association (unpublished).

IFPRI (2000). Pilot analysis of global ecosystems (PAGE): Agroecosystems dataset. 2000. International Food Policy Research Institute (IFPRI), Washington, DC.

Ismunadji, M. and Soepardi, G. (1984). Peat soils problems and crop production. p. 489-502. In *Organic Matter and Rice*. International Rice Research Institute, Los Banos.

ISSS-ISRIC-FAO (1998). *World Reference Base for Soil Resources*. Acco Press, Leuven, Belgium.

Jahiruddin, M. and Cresser, M.S. (1997). Sequential cold and hot water extraction of boron from soils and re-extraction after adsorption by bentonite, kaolinite, iron, and aluminium hydrous oxides over a range of pH. Communications in Soil Science and Plant Analysis 28: 1643-1652.

Jarvis, S.C. (1981). Copper concentrations in plants and their relationship to soil properties. p. 265-285. In J.F. Loneragan, A.D. Robson and R.D. Graham (eds.), *Copper in Soils and Plants*. Academic Press, London.

Jin, J.Y., Martens, D.C. and Zelazny, L.W. (1987). Distribution and plant availability of soil boron fractions. Soil Science Society of America Journal 51: 1228-1231.

Jin, J., Ping, H. and Shihua, T. (2006). Micronutrient deficiencies occurrence and correction: The Chinese example. In *Optimizing Resource Use Efficiency for Sustainable Intensification of Agriculture*. IFA Agriculture Conference, 27 February to 2 March 2006, Kunming, PR China.

Johansen, C., Kerridge, P.C. and Sultana, A. (1997). Responses of forage legumes and grasses to molybdenum. p. 202-228. In U.C. Gupta (ed.), *Molybdenum in Agriculture*. Cambridge University Press, Cambridge.

Johansen, C., Musa, A.M., Kumar Rao, J.V.D.K., Harris, D., Ali, M.Y., Lauren, J.G. (2005). Molybdenum response of chickpea in the High Barind Tract of Bangladesh and in Eastern India. p. 205–220. In P. Andersen, J.K. Tuladhar, K.B. Karki, S.L. Maskey (eds.), *Micronutrients in South and South East Asia*. Proceedings of an International Workshop held 8–11 September 2004, Kathmandu, Nepal. International Centre for Integrated Mountain Development, Kathmandu, Nepal.

Johansen, C., Musa, A.M., Kumar Rao, J.V.D.K., Harris, D.M., Ali, Y., Shahidullah, A.K.M. and Lauren, J.G. (2007). Correcting molybdenum deficiency of chickpea in the High Barind Tract of Bangladesh. Journal of Plant Nutrition and Soil Science 170: 752-761.

Johnson, M.A. (1998). Copper: physiology, dietary sources and requirements. p. 442-450. In *Encyclopedia of Human Nutrition*. Academic Press, London.

Johnson, S.E., Lauren, J.G., Welch, R.M. and Duxbury, J.M. (2005). A comparison of the effects of micronutrient seed priming and soil fertilization on the mineral nutrition of chickpea (*Cicer arietinum*), lentil (*Lens culinaris*), rice (*Oryza sativa*) and wheat (*Triticum aestivum*) in Nepal. Experimental Agriculture 41: 427-448.

Jones, G.B. and Belling, G.B. (1967). The movement of copper, molybdenum and selenium in soils as indicated by radioactive isotopes. Australian Journal of Agricultural Research 18: 733-740.

Jones, J.B. (ed.) (1982). Proceedings of the First International Symposium on Iron Nutrition and Interactions in Plants. Journal of Plant Nutrition 5: 229-1001.

Jones, J.B. (ed.) (1984). Proceedings of the Second International Symposium on Iron Nutrition and Interactions in Plants. Journal of Plant Nutrition 7: 1-1774.

Jones, J.B (ed.) (1986). Proceedings of the Third International Symposium on Iron Nutrition and Interactions in Plants. Journal of Plant Nutrition 9: 161-1076.

Jones, J.B (ed.) (1988). Proceedings of the Fourth International Symposium on Iron Nutrition and Interactions in Plants. Journal of Plant Nutrition 11: 605-1621.

Jones, J.B. (1993). Review of perspective, issues, and trends in soil and plant testing in the United States of America. Australian Journal of Experimental Agriculture 33: 973-978.

Jones, J.B., Wolf, B. and Mills, H.A. (1991). *Plant Analysis Handbook*. Micro-Macro Publishing, Athens, Georgia.

Kaiser, B.N., Gridley, K.L., Brady, J.N., Phillips, T. and Tyerman, D. (2005). The role of molybdenum in agricultural plant production. Annals of Botany 96: 745-754.

Kang, B.T. and Osiname, O.A. (1985). Micronutrient problems in tropical Africa. Fertilizer Research 7: 131-150.

Karamanos, R.E., Walley, F.L. and Flaten, P.L. (2005). Effectiveness of seed row placement of granular copper products for wheat. Canadian Journal of Soil Science 85: 295-306.

Kataki, P.K., Srivastava, S.P., Saifuzzaman, M. and Upreti, H.K. (2001). Sterility in wheat and response of field crops to applied boron in the Indo-Gangetic plains. Journal of Crop Production 4: 133-165.

Katyal, J.C. and Vlek, P.L.G. (1985). Micronutrient problems in tropical Asia. Fertilizer Research 7: 69-94.

Keen, C.L. and Zidenberg-Cherr, S. (1999). Manganese. p.3686-3691. In *Encyclopedia of Food Sciences and Nutrition*. Academic Press, Amsterdam.

Keen, C.L., Ensunsa, J.L. and Watson, M.H. (1999). Nutritional aspects of manganese from experimental studies. Neurotoxicology 20: 213-223.

Kirk, G. (2004). *The Biogeochemistry of Submerged Soils*. John Wiley and Sons, Chichester.

Kirk, G.J. and Loneragan, J.F. (1988). Functional boron requirement for leaf expansion and its use as a critical value for diagnosis of boron deficiency in soybean. Agronomy Journal 80: 758-762.

Kochian, L.V. (1991). Mechanisms of micronutrient uptake and translocation in plants. p. 229-296. In J.J. Mortvedt, F.R. Cox, L.M. Shuman and R.M. Welch (eds.), *Micronutrients in Agriculture*. 2nd ed. SSSA Book Series No. 4. Soil Science Society of America, Madison, Wisconsin.

Kotur, S.C. (1991). Effect of boron, lime and their residue on yield of cauliflower, leaf composition and soil properties. p. 349-354. In R.J. Wright (ed.), *Plant-Soil Interactions at Low pH*. Kluwer Academic Publishers, Dordrecht.

Kumar, S. and Sharma, J.P. (1997). Exogenous application of boron and nitrogen on susceptibility of cauliflower to black rot. Journal of Mycology and Plant Pathology 27: 210-214.

Ladha, J.K., Pathak, H., Padre-Tirol, A. and Dawe, D. (2003). Productivity trends in intensive rice-wheat cropping systems in Asia. p. 45-76. In J.K. Ladha, J.E. Hill, J.M. Duxbury, R.K. Gupta and R.J. Buresh (eds.), *Improving the Productivity and Sustainability of Rice-Wheat Systems: Issues and Impacts*. ASA Special Publication No. 65.

Lee, J., Masters, D.G., White, C.L., Grace, N.D. and Judson, G.J. (1999). Current issues in trace element nutrition of grazing livestock in Australia and New Zealand. Australian Journal of Agricultural Research 50: 1341-1364.

Leggett, G.E. and Westermann, D.T. (1986). Effect of corn, sugarbeets, and fallow on zinc availability to subsequent crops. Soil Science Society of America Journal 50: 963-968.

Leite, V.M., Brown, P.H. and Rosolem, C.A. (2007). Boron translocation in coffee trees. Plant and Soil 290: 221-229.

León, L.A., López, A.S. and Vlek, P.L.G. (1985). Micronutrient problems in tropical Latin America. Fertilizer Research 7: 95-119.

Li B.H., Li, W.H., Kui, M.C., Chao, W.S, Jern, H.P., Li, C.R., Chu, W.J. and Wang, C.L. (1978). Studies on the cause of sterility of wheat (in Chinese with English abstract). Journal Northeast Agricultural College 3: 1-19.

Lindsay, W.L. (1991). Inorganic equilibria affecting micronutrients in soils. p. 89-112. In J.J. Mortvedt, F.R. Cox, L.M. Shuman and R.M. Welch (eds.), *Micronutrients in Agriculture*. 2nd ed. SSSA Book Series No. 4. Soil Science Society of America, Madison, Wisconsin.

Lindsay, W.L. and Norvell, W.A. (1978). Development of a DTPA soil test for zinc, iron, manganese and copper. Soil Science Society of America Journal 42: 421-428.

Liu, Z. (1992). Characterization of content and distribution of micronutrients in soils of China. p. 54-62. In S. Portch (ed.), *Role of S, Mg and Micronutrients in Balanced Plant Nutrition*. Potash and Phosphate Institute, Hong Kong.

Loneragan, J.F. (1988). Distribution and movement of manganese in plants. p. 113-124. In R.D. Graham, R.J. Hannam and N.C. Uren (eds.), *Manganese in Soils and Plants*. Kluwer Academic Publishers, Dordrecht.

Loneragan, J.F., Kirk, G.J. and Webb, M. J. (1987). Translocation and function of zinc in roots. Journal of Plant Nutrition 10: 1247-1254.

Loneragan, J.F., Robson, A.D. and Graham, R.D. (eds.) (1981). *Copper in Soils and Plants*. Academic Press, Sydney.

Longnecker, N., Crosbie, J., Davies, F. and Robson, A.D. (1996). Low seed manganese concentration and decreased emergence of *Lupinus angustifolius*. Crop Science 36: 355-361.

Lucena, J.J. (2003). Fe chelates for remediation of Fe chlorosis in strategy I plants. Journal of Plant Nutrition 26: 1969-1984.

Lucena, J.J. (2006). Synthetic iron chelates to correct iron deficiency in plants. p.103-128. In L.L. Barton and J. Abadia (eds.), *Iron Nutrition in Plants and Rhizospheric Microorganisms*, Springer, Dordrecht.

Lucena, J.J., Sentis, J.A., Villen, M., Lao, T. and Perez-Saez, M. (2008). IDHA chelates as a micronutrient source for green bean and tomato in fertigation and hydroponics. Agronomy Journal 100: 813-818.

Lynch, S.R. (2003a). Iron-deficiency anemia. p. 215-220. In *Encyclopedia of Food Sciences and Nutrition*. Academic Press, Amsterdam.

Lynch, S.R. (2003b). Iron/Physiology. p. 3373-3379. In *Encyclopedia of Food Sciences and Nutrition*. Academic Press, Amsterdam.

Machota, J.E. and Hopper, F.L. (2001). Influence of terbufos and nicosulfuron on iron chlorosis and growth of corn. Journal of Plant Nutrition 24: 1445-1455.

Marschner, H. (1993). Zinc uptake from soils. p. 59-77. In A.D. Robson (ed.), *Zinc in Soils and Plants*. Kluwer Academic Press, Dordrecht.

Marschner, H. (1995). *Mineral Nutrition of Higher Plants*. Academic Press, London.

Martens, D.C. and Lindsay, W.L. (1990). Testing soils for copper, iron, manganese, and zinc. p. 229-273. In R.L. Westermann (ed.), *Soil Testing and Plant Analysis*. 3rd ed. SSSA Book Series No. 3. Soil Science Society of America, Madison, Wisconsin.

Martens, D.C. and Westermann, D.T. (1991). Fertilizer applications for correcting micronutrient deficiencies. p. 297-328. In J.J. Mortvedt, F.R. Cox, L.M. Shuman and R.M. Welch (eds.), *Micronutrients in Agriculture*. 2nd ed. SSSA Book Series No. 4. Soil Science Society of America, Madison, Wisconsin

Materne, M., McMurray, L., Nitschke, S., Regan, K., Heuke, L., Dean, G. and Carpenter, D. (2002). The future of Australian lentil production. p. 14-18. In J.B. Brouwer (ed.), *Proceedings of Lentil Focus 2002*. Victorian Department of Primary Industries, Horsham.

Matoh, T. (1997). Boron in plant cell walls. Plant and Soil 193: 59-70.

Matsi, T., Antoniadis, V. and Barbayiannis, N. (2000). Evaluation of the NH_4HCO_3 DTPA soil test for assessing boron availability to wheat. Communications in Soil Science and Plant Analysis 31: 669-678.

McBeath, T.M., Armstrong, R.A., Lombi, E., McLaughlin, M.J. and Holloway R.E. (2005). Responsiveness of wheat (*Triticum aestivum*) to liquid and granular phosphorus fertilisers in southern Australian soils. Australian Journal Soil Research 43: 203-212.

McBride, M.B. (1981). Forms and distribution of copper in solid and solution phases of soil. p. 25-46. In J.F. Loneragan, A.D. Robson and R.D. Graham (eds.), *Copper in Soils and Plants*. Academic Press, Sydney.

McDowell, L.R. (2003). *Minerals in Animal and Human Nutrition*. 2nd ed. Elsevier Science BV, Amsterdam.

McFarlane, J.D. (1999). Iron. p. 295-301. In K.I. Peverill, L.A. Sparrow and D.J. Reuter (eds.), *Soil Analysis. An Interpretation Manual*. CSIRO Publishing, Collingwood.

McGrath, S.P. and Loveland, P.J. (1992). *Soil Geochemical Atlas of England and Wales*. Blackie Academic and Professional, Glasgow.

McGuire, M. and Beerman, K.I.A. (2007). *Nutritional Sciences: From Fundamentals to Food*. Thomson/Wadsworth.

McHargue, J.S. (1922). The role of manganese in plants. Journal of the American Chemical Society 44: 1592.

McKenzie, R.M. (1980). The adsorption of lead and other heavy metals on oxides of manganese and iron. Australian Journal of Soil Research 19: 41-50.

McLaren, R.G and Crawford, D.V. (1973). Studies on soil copper. I. The fractionation of copper in soils. Journal of Soil Science 24: 172-181.

McLaughlin, M.J., Reuter, D.J. and Rayment, G.E. (1999). Soil testing-Principles and Concepts. p. 1-21. In K.I. Peverill, L.A. Sparrow and D.J. Reuter (eds.), *Soil Analysis. An Interpretation Manual*. CSIRO Publishing, Collingwood.

McLay, L.D. and Robson, A.D. (1992). The effect of chlorsulfuron and diclofop methyl on the uptake and utilization of zinc by wheat. Australian Journal of Agricultural Research 43: 59-65.

Mendel, R.R. and Haensch, R. (2002). Molybdoenzymes and molybdenum cofactor in plants. Journal of Experimental Botany 53: 1689-1698.

Mengel, K. and Kirkby, E.A. (2001). *Principles of Plant Nutrition*. Kluwer Academic Publishers, Dordrecht.

Moraghan, J.T. and Mascagni Jr, H.J. (1991). Environmental and soil factors affecting micronutrient deficiencies and toxicities. p. 371-425. In J.J. Mortvedt, F.R. Cox, L.M. Shuman and R.M. Welch (eds.), *Micronutrients in agriculture*. 2nd ed. SSSA Book Series No. 4. Soil Science Society of America, Madison, Wisconsin.

Moran, K. (2004). Micronutrient product types and their development. Proceedings No. 545. International Fertiliser Society, York, UK.

Moran, K. (2006). Main micronutrient forms/ products available and methods of application. 2006 IFA Agricultural Conference – Workshop on micronutrients, Kunming, China, 27 Feb. – 2 March 2006.

Morrill, L.G., Hill, W.E., Chrudinsky, W.A., Ashlock, L., Trip, L.D., Tucker, B.B. and Weatherly, L. (1977). Boron requirements of Spanish peanuts in Oklahoma: effects on yield and quality and interaction with other nutrients. Agricultural Experimental Station, Oklahoma State University, MP-99.

Mortvedt, J.J. (1985a). Micronutrient fertilizers and fertilization practices. Fertilizer Research 7: 221-235.

Mortvedt, J.J. (1985b). Plant uptake of heavy metals in zinc fertilizers made from industrial by-products. Journal of Environmental Quality 14: 424–427.

Mortvedt, J.J. (1991). Micronutrient fertilizer technology. p. 523-548. In J.J. Mortvedt, F.R. Cox, L.M. Shuman and R.M. Welch (eds.), *Micronutrients in Agriculture*. 2nd ed. SSSA Book Series No. 4. Soil Science Society of America, Madison, Wisconsin.

Mortvedt, J.J. (1994). Needs for controlled-availability micronutrient fertilizers. Fertilizer Research 38: 213-221.

Mortvedt, J.J. (1996). Heavy metal contaminants in inorganic and organic fertilizers. Fertilizer Research 43: 55-61.

Mortvedt, J.J. (1997). Sources and methods for molybdenum fertilization of crops. p. 171-201. In U.C. Gupta (ed.), *Molybdenum in Agriculture*. Cambridge University Press, New York.

Mortvedt, J.J. and R.J. Gilkes. (1993). Zinc fertilizers. p. 33-44. In A.D. Robson (ed.), *Zinc in Soils and Plants*. Kluwer Academic Publications, Dordrecht.

Mortvedt, J.J., Cox, F.R., Shuman, L.M. and Welch, R.M. (eds.), (1991). *Micronutrients in Agriculture*. 2nd ed. SSSA Book Series No. 4. Soil Science Society of America, Madison, Wisconsin.

Nable, R.O. and Webb, M.J. (1993). Further evidence that Zn is required throughout the root zone for optimal plant growth and development. Plant and Soil 150: 247-253.

NASAA (2004). Organic Standard. December 2004, Amended 13th May, 2008. National Association for Sustainable Agriculture Australia Limited, Stirling, South Australia.

Nayyar, V.K., Arora, C.L. and Kataki, P.K. (2001). Management of soil micronutrients deficiencies in the rice-wheat cropping system. Journal of Crop Production 4: 87-131.

Netsangtip, R., Bell, R.W., Dell, B. and Loneragan, J.F. (1993). An effect of light on the B requirement for leaf blade elongation in black gram (*Vigna mungo*). Plant and Soil 155/156: 413-416.

Neumann, P.M. (2004). Foliar nutrition of protected crops. Proceedings International Fertiliser Society 524: 1-12.

New Ag International (2003). Micronutrients: focus on boron. September 2003. NAI Ltd., Colmar.

New Ag International (2007). The market for micronutrient copper. March 2007. NAI Ltd., Colmar.

Nielsen, F.H. (1984). Ultratrace elements in nutrition. Annual Reviews in Nutrition 4: 646-658.

Nielsen, F.H. (1997). Boron in human and animal nutrition. Plant and Soil 193: 199-208.

Nielsen, F.H. (1999). Ultratrace minerals. p. 283-303. In M. Shils, J.A. Olson, M. Shike and A.C. Ross (eds.), *Nutrition in Health and Disease*. 9th ed. Williams & Wilkins, Baltimore.

Nielsen, F.H. (2002). The nutritional importance and pharmacological potential of boron for higher animals and human. p. 37-49. In H.E. Goldbach, B. Rerkasem, M.A. Wimmer, P.H. Brown, M. Thellier and R.W. Bell (eds.), B*oron in Plant and Animal Nutrition*. Kluwer Academic Publishers, Dordrecht.

Noppakoonwong, R.N., Rerkasem, B., Bell, R.W., Dell, B. and Loneragan, J.F. (1997). Prognosis and diagnosis of boron deficiency in blackgram (Vigna mungo L. Hepper) in the field by using plant analysis. p. 89-93. In R.W. Bell and B. Rerkasem (eds.), *Boron in Soils and Plants*. Proceedings of the International Symposium on Boron in Soils and Plants, Chiang Mai, Thailand, 7-11 September 1997. Developments in Plant and Soil Sciences, 76. Kluwer Academic Publishers, Dordrecht.

Nott, H., Falloon, R. and Cheah, L.H. (1999). Clubroot control from safe chemicals. Commercial Grower 54: 24-26.

O'Neill, M.A., Ishii, T., Albersheim, P. and Darvill, A.G. (2004). Rhamnogalacturonan II: structure and function of a borate cross-linked cell wall pectic polysaccharide. Annual Review of Plant Biology 55:109-139.

Osborne, L.D., Robson, A.D and Bowran, D.G. (1993). The impact of chlorsulfuron and diclofop-methyl on nutrient uptake by wheat. Australian Journal of Agricultural Research 44: 1757-1766.

Pal, S., Datta, S.P., Rattan, R.K. and Singh, A.K. (2008). Diagnosis and amelioration of iron deficiency under aerobic rice. Journal of Plant Nutrition 31: 919-940.

Papadakis, I.E., Protopapadakis, E., Therios, I.N. and Tsirakoglou, V. (2005). Foliar treatments of Mn deficient 'Washington navel' orange trees with two Mn sources. Scientia Horticulturae 106: 70-75.

Parker, D.R. and Gardner, E.H. (1982). Factors affecting the mobility and plant availability of boron in some Western Oregon soils. Soil Science Society of America Journal 46: 573-578.

Parker, D.R. and Norvell, W.A. (1999). Advances in solution culture methods for plant mineral nutrition research. Advances in Agronomy 65: 151–213.

Paull, J.G., Bell, R.W. and Materne, M.A. (2005). Nutrient efficiency in food legumes. In *Proceedings Fourth International Food Legumes Research Conference (IFLRC-IV) on Food Legumes for Nutritional Security and Sustainable Agriculture*, October 18 to 22, 2005 at IARI, New Delhi.

Peryea, F.J. and Lageschulte, J.M. (2000). Boron fertilizer product and concentration influence spray water pH. HortTechnology 10: 350-353.

Pestana, M., Correia, P.J., de Varennes, A., Abadía, J. and Faria, E.A. (2001). Effectiveness of different foliar iron applications to control iron chlorosis in orange trees grown on a calcareous soil. Journal of Plant Nutrition 24: 613-622.

Peverill, K.I. (1993). Soil testing and plant analysis in Australia. Australian Journal of Experimental Agriculture 33: 963-971.

Peverill, K.I., Sparrow, L.A. and Reuter, D.J. (eds.) (1999). *Soil Analysis. An Interpretation Manual*. CSIRO Publishing, Collingwood.

Phillips, M.R. (2006). Economic benefits from using micronutrients for the farmer. In *Optimizing Resource Use Efficiency for Sustainable Intensification of Agriculture*. IFA Agriculture Conference, Kunming, PR China. 27 February to 2 March 2006.

Pinyerd, C.A., Odum, J.W., Long, F.L. and Dane, J.H. (1984). Boron movement in a Norfolk loamy sand. Soil Science 137: 428-433.

Power, P.F. and Woods, W.G. (1997). The chemistry of boron and its speciation in plants. Plant and Soil 193: 1-13.

Pregno, L.M. and Armour, J.D. (1992). Boron deficiency and toxicity in potato cv. Sebago on an oxisol of the Atherton Tablelands, North Queensland. Australian Journal of Experimental Agriculture 32: 251-253.

Price, G. (ed.) (2006). *Australian Soil Fertility Manual*. 3rd ed. Fertilizer Industry Federation of Australia and CSIRO, Melbourne.

Rainey, C. J., Nyquist, L. A., Coughlin, J.R. and Downing, R.G. (2002). Dietary boron intake in the United States: CSFII 1994-1996. Journal Food Composition Analysis 15: 237-250.

Raïsänen, M., Repo, T. and Lehto, T. (2007). Cold acclimation was partially impaired in boron deficient Norway spruce seedlings. Plant and Soil 292: 271-282.

Ram, S., Bist, L.D. and Sirohi, S.C. (1989). Internal fruit necrosis of mango and its control. Acta Horticulturae 231: 805-813.

Rashid, A. (2006). Incidence, diagnosis and management of micronutrient deficiencies in crops: Success stories and limitations in Pakistan. In *Optimizing Resource Use Efficiency for Sustainable Intensification of Agriculture*. IFA Agriculture Conference, Kunming, PR China. 27 February to 2 March 2006.

Rashid, A. and Ryan, J. (2004). Micronutrient constraints to crop production in soils with Mediterranean-type characteristics: A review. Journal of Plant Nutrition 27: 959-975.

Ratto de Miguez, S., Diggs, C. and Ras, C. (1999). Effect of some soil properties on extractable boron content in Argentine Pampas soils. Communications in Soil Science and Plant Analysis 30: 2083-2100.

Rawson, H.M. (1996). Hypothesis for why sterility occurs in wheat in Asia. p 132-134. In H.M. Rawson and K.D. Subedi (eds.), *Sterility in Wheat in Sub-tropical Asia: Extent, Causes and Solutions*. ACIAR proceedings No. 72. Australian Centre for International Agricultural Research, Canberra.

Ray, S.K., Varadachari, C. and Ghosh, K. (1997). Novel slow-releasing micronutrient fertilizers. 2. Copper compounds. Journal of Agricultural and Food Chemistry 45: 1447-1453.

Rayman, M.P. (2005). Selenium in cancer prevention: a review of the evidence and mechanism of action. Proceedings of the Nutrition Society 64: 527-542.

Reddy, K.J., Munn, L.C. and Wang, L. (1997). Chemistry and mineralogy of molybdenum in the terrestrial environment. p. 4-22. In U.C. Gupta (ed.), *Molybdenum in Agriculture*. Cambridge University Press, Cambridge.

Reisenauer, H.M. (1960). Cobalt in nitrogen fixation by a legume. Nature 186: 375-376.

Reisenauer, H.M. (1988). Determination of plant-available soil manganese. p. 87-98. In R.D. Graham, R.J. Hannam and N.C. Uren (eds.), *Manganese in Soils and Plants*. Kluwer Academic Publishers, Dordrecht.

Rengel, Z. (1997). Root exudation and microflora populations in rhizosphere of crop genotypes differing in tolerance to micronutrient deficiency. Plant and Soil 196: 255-260.

Rengel, Z. (2001). Genotypic differences in micronutrient use efficiency in crops Communications in Soil Science and Plant Analysis 32: 1163-1186.

Rengel, Z. and Graham, R.D. (1995). Importance of seed zinc content for wheat growth on zinc-deficient soil. I. Vegetative growth. Plant and Soil 173:259-266.

Rerkasem, B. (1996a). Boron and plant reproductive development. p. 32-35. In H.M. Rawson and K.D. Subedi (eds.), *Sterility in Wheat in Subtropical Asia: Extent, Causes* *and Solutions*. ACIAR proceedings No. 72. Australian Centre for International Agricultural Research, Canberra.

Rerkasem, B. (1996b). A general survey of the incidence of wheat sterility. p. 8-12. In H.M. Rawson and K.D. Subedi (eds.), *Sterility in Wheat in Subtropical Asia: Extent, Causes and Solutions*. ACIAR Proc. No. 72. Australian Centre for International Agricultural Research, Canberra.

Rerkasem, B. and Jamjod, S. (2001). Overcoming wheat sterility problem with boron efficiency. p. 82-83. In W. Horst, M.K. Schenk, A. Burkert, N. Claasen, H. Flessa, W.B. Frommer, H. Goldbach, H-W. Olfs, V. Römheld, B. Sattelmacher, U. Schmidhalter, S. Schubert, N. von Wiren and L. Wittenmayer (eds.), *Plant Nutrition Food Security and Sustainability of Agro-ecosystems through Basic and Applied Research*, Developments in Plant and Soil Sciences 92. Kluwer Academic Publishers, Dordrecht.

Rerkasem, B. and Jamjod, S. (2004). Boron deficiency in wheat: a review. Field Crops Research 89: 173-186.

Rerkasem, B. and Loneragan, J.F. (1994). Boron deficiency in two wheat genotypes in a warm, subtropical region. Agronomy Journal 86: 887-890.

Rerkasem, B., Saunders, D.A. and Dell, B. (1989). Grain set failure and boron deficiency in wheat in Thailand. Journal of Agriculture (Chiang Mai University) 5: 1-10.

Rerkasem, B., Bell, R.W., Lordkaew, S. and Loneragan, J.F. (1993). Effects of seed and soil boron on early seeding growth of black and green gram. p. 281-285. In M.L. van Beusichem (ed.), *Plant Nutrition - Physiology and Applications*. Kluwer Academic Publishers, Dordrecht.

Rerkasem, B., Bell, R.W., Lordkaew, S. and Loneragan, J.F. (1997). Relationship of seed boron concentration to germination and growth of soybean (*Glycine max* L. Merr.). Nutrient Cycling in Agro-ecosystems 48: 217-223.

Rerkasem, B., Netsangtip, R., Bell, R.W. and Loneragan, J.F. (1988). Comparative species responses to boron on a Typic Tropaqualf in Northern Thailand. Plant and Soil 106: 15-21.

Reuter, D.J. and Robinson, J.B. (eds.) (1997). P*lant Analysis. An Interpretation Manual*. CSIRO Publishing, Collingwood.

Reuter, D.J., Alston, A.M. and McFarlane, J.D. (1988). Occurrence and correction of manganese deficiency. p. 205-224. In R.D. Graham, R.J. Hannam and N.C. Uren (eds.), *Manganese in Soils and Plants*. Kluwer Academic Publishers, Dordrecht.

Riley, M.M., Robson A.D., Gartrell, J.W. and Jeffrey, R.C. (1987). The absence of leaching of molybdenum in acidic soils from Western Australia. Australian Journal of Soil Research 25: 179-184.

Robson, A.D. (ed.) (1993). *Zinc in Soils and Plants*. Kluwer Academic Publishers, Dordrecht.

Robson, A. D. and Mead, G.R. (1980). Seed cobalt in *Lupinus angustifolius*. Australian Journal of Agricultural Research 31: 109-116.

Robson, A. D. and Pitman, M.G. (1983). Interactions between nutrients in higher plants. p. 147-180. In A. Lauchli and R.L. Bieleski (eds.), *Encyclopedia of Plant Physiology*. New Series Vol 15B. Springer-Verlag, Berlin.

Robson, A. D. and Snowball, K. (1987). Response of narrow-leaf lupins to cobalt application in relation to cobalt concentration in seed. Australian Journal of Experimental Agriculture 27: 657-660.

Rocha, M. (2006). Micronutrient consumption in Brazil (personal communication). ANDA's Statistics Committee on Micronutrients, 2008. Sao Paulo, Brazil.

Rombolà, A.D., Dallari, S., Quartieri, M. and Scudellari, D. (2002). Effect of foliar-applied Fe sources, organic acids and sorbitol on the re-greening of kiwifruit leaves affected by lime-induced iron chlorosis. Acta Horticulturae 594: 349-355.

Römheld, V. and Marschner, H. (1986). Mobilization of iron in the rhizosphere of different plant species. p. 155-204. In B. Tinker and A. Lauchli (eds.), *Advances in Plant Nutrition Vol. 2*, Praeger Scientific, New York.

Rosolem, C.A. and Sacramento, L.V.S. (2001). Efficiency of foliar Zn fertilizers in coffee and citrus. p. 704-705. In W. Horst, M.K. Schenk, A. Burkert, N. Claasen, H. Flessa, W.B. Frommer, H. Goldbach, H-W. Olfs, V. Römheld, B. Sattelmacher, U. Schmidhalter, S. Schubert, N. von Wiren and L. Wittenmayer (eds.), *Plant Nutrition Food Security and Sustainability of Agro-ecosystems through Basic and Applied Research*. Developments in Plant and Soil Sciences 92. Kluwer Academic Publishers, Dordrecht.

Rutherford, A.W. and Boussac, A. (2004). Water photolysis in biology. Science 303: 1782-1783.

Saarela, I. (1985). Plant-available boron in soils and the boron requirement of spring oilseed rapes. Annales Agriculturae Fenniae 24: 183-265.

Sachs, J. (1860). Berichte über die physiologische Tätigkeit an der Versuchsstation in Tharandt. IV. Vegetationsversuche mit Ausschluss des Bodens über die Nährstoffe und sonstigen Ernährungsbedingungen von Mais, Bohnen und anderen Pflanzen. Landwirtschafts Versuchsstation 2: 219-268.

Saeki, K., Kunito, T., Oyaizu, H. and Matsumoto, S. (2002). Relationships between baterial tolerance levels and forms of copper and zinc in soils. Journal of Environmental Quality 31: 1570-1575.

Sakal, R., Singh, B.P., Singh A.P. and Sinha, R.B. (1985). Critical limit of boron in soils and plant for the response of black gram to applied boron in calcareous soil. Journal Indian Society of Soil Science 33: 725-727.

Sandstrom, B. and Lonnerdal, B. (1989). Promoters and antagonists of zinc absorption. p. 57-78. In C.F. Mills (ed.), *Zinc in Human Biology*. Springer-Verlag, New York.

Sarkar, D., Mandal, B. and Kundu, M.C. (2007). Increasing use efficiency of boron fertilisers by rescheduling the time and methods of application for crops in India. Plant and Soil 301: 77-85.

Sauer, P. and Frebort, I. (2003). Molybdenum cofactor-containing oxireductase family in plants. Biologia Plantarum 46: 481-490.

Schaafsma, A., de Vries, P.J.F. and Saris, W.H.M. (2001). Delay of natural bone loss by higher intakes of specific minerals and vitamins. Critical Reviews in Food Science and Nutrition 41: 225-249.

Sharma, C.P. (2006). *Plant Micronutrients*. Science Publishers, Enfield.

Shaviv, A. (2001). Advances in controlled-release fertilizers. Advances in Agronomy 17: 1-49.

Shivay, Y.S., Kumar, D., Prasad, R. and Ahlawat, I.P.S. (2008). Relative yield and zinc uptake by rice from zinc sulphate and zinc oxide coatings onto urea. Nutrient Cycling in Agroecosystems 80: 181-188.

Shorrocks, V.M. (1991a). Boron - A global appraisal of the occurrence, diagnosis and correction of boron deficiency. p. 39-53. In S. Portch (ed.), *Proceedings of the International Symposium of S, Mg, and Micronutrients in Balanced Plant Nutrition*. Potash and Phosphate Institute, Hong Kong.

Shorrocks, V.M. (1991b). Micronutrients-requirements use and recent developments. p. 391-412. In S. Portch (ed.) *Proceedings of the International Symposium of S, Mg, and Micronutrients in Balanced Plant Nutrition*. Potash and Phosphate Institute, Hong Kong.

Shorrocks, V. M. (1997). The occurrence and correction of boron deficiency. Plant and Soil 193: 121-148.

Shorrocks, V.M. and Nicholson, D.D. (1980). The influence of boron deficiency on fruit quality. p. 103-108. In D. Atkinson, J.E. Jackson, R.O. Sharples and W.M. Waller, (eds.), *Mineral Nutrition of Fruit Trees*. Butterworths, London.

Shuman, L.M. (1979). Zinc, manganese and copper soil fractions. Soil Science 127: 10-17.

Shuman, L.M. (1991). Chemical form of micronutrients in soils. p. 113-144. In J.J. Mortvedt, F.R. Cox, L.M. Shuman and R.M. Welch (eds.), *Micronutrients in Agriculture*. 2nd ed. SSSA Book Series No. 4. Soil Science Society of America, Madison, Wisconsin.

Siba, P., Datta, R., Rattan, R.K., Suribabu, K. and Datta, S.C. (2002). Fractionation and calorimetric determination of boron in soils. Journal of Plant Nutrition and Soil Science 165: 179-184.

Siddiqui, I.A., Shaukat, S.S. and Hamid, M. (2002). Role of zinc in rhizobacteria-mediated suppression of root-infecting fungi and root-knot nematode. Journal of Phytopathology 150: 569-575.

Sillanpää, M. (1982). *Micronutrients and the Nutrient Status of Soils: a Global Study*. Soils Bulletin 48, FAO, Rome.

Sillanpää, M. (1990). *Micronutrient Assessment at Country Level: An International Study*. FAO Soils Bulletin No. 63, FAO, Rome.

Silverberg, J., Young, R.D. and Hoffmeister Jr, G. (1972). Preparation of fertilizers containing micronutrients. p. 431-458. In J.J. Mortvedt, F.R. Cox, L.M. Shuman and R.M. Welch (eds.), *Micronutrients in Agriculture.* 1st ed. Soil Science Society of America, Madison, Wisconsin.

Simoglou, K.B. and Dordas, C. (2006). Effect of foliar applied boron, manganese and zinc on tan spot in winter durum wheat. Crop Protection 25: 657-663.

Sims, J.T. and Eizazi, F. (1997). Testing for molybdenum availability in soils. p. 111-130. In U.C. Gupta (ed.), *Molybdenum in Agriculture*. Cambridge University Press, Cambridge.

Sims, J.T. and Johnson, G.V. (1991). Micronutrient soil tests. p. 427-476. In J.J. Mortvedt, F.R. Cox, L.M. Shuman and R.M. Welch (eds.), *Micronutrients in Agriculture*. 2nd ed. SSSA Book Series No. 4. Soil Science Society of America, Madison, Wisconsin.

Singh, A.L., Basu, M.S. and Singh, N.B. (2004). *Mineral Disorders of Groundnut*. National Research Centre for Groundnut, Junagadh.

Singh, K., Mori, S. and Welch, R.M. (2001). *Perspectives on the Micronutrient Nutrition of Crops*. Scientific Publishers (India), Jodhpur.

Singh, M.V. (2004). Transfer of scientific knowledge to usable field practices. In Proceedings of IFA Symposium on Micronutrients. 22-25 February 2004, Dehli, India. International Fertilizer Industry Association (IFA), Paris.

Singh, M.V. (2008). Micronutrient deficiencies in crops and soils of India. p. 93-125. In B.J. Alloway (ed.), *Micronutrient Deficiencies in Global Crop Production*. Springer, Dordrecht.

Slaton, N.A., Gbur Jr, E.E., Wilson, C.E. and Norman, R.J. (2005). Rice response to granular zinc sources varying in water-soluble zinc. Soil Science Society of America Journal 69: 443-452.

Smith, B.H. and Leeper, G.W. (1969). The fate of applied molybdenum in acidic soils. Journal of Soil Science 20: 246-254.

Smith, F.W. and Loneragan, J.F. (1997). Interpretation of plant analysis: concepts and principles. p. 1-33. In D.J. Reuter and J.B. Robinson (eds.), *Plant Analysis. An Interpretation Manual.* CSIRO Publishers, Melbourne.

Smith, T.E., Stephenson, R.A., Asher, C.J. and Hetherington, S.E. (1997). Boron deficiency in avocado. 2. Effects on fruit size and ripening. p. 135-138. In R.W. Bell and B. Rerkasem (eds.) *Boron in Soils and Plants*. Proceedings of the International Symposium on Boron in Soils and Plants, held at Chiang Mai, Thailand, 7-11 September, 1997. Developments in Plant and Soil Sciences Vol. 76. Kluwer Academic Publishers, Dordrecht, The Netherlands.

Soil Survey Staff (1998). *Keys to Soil Taxonomy*. USDA Natural Resources Conservation Service, Washington.

Sommer, A.L. (1931). Copper as an essential element for plant growth. Plant Physiology 6: 339-345.

Sommer, A.L. and Lipman, C.B. (1926). Evidence on the indispensible nature of zinc and boron for higher green plants. Plant Physiology 1: 231-249.

Sparks, D.L. (2003). *Environmental Soil Chemistry*. 2nd ed. Academic Press, Amsterdam.

Sparrow, D.H. and Graham, R.D. (1988). Susceptibility of zinc-deficient wheat plants to colonization by *Fusarium graminearum* Schw. Group 1. Plant and Soil 112: 261-266.

Srivastava, P.C. and Gupta, U.C. (1996). *Trace Elements in Crop Production*. Science Publishers, Enfield.

Srivastava, S.P., Bhandari, T.M.S., Yadav, C.R., Joshi, M. and Erskine, W. (2000). Boron deficiency in lentil: Yield loss and geographic distribution in a germplasm collection. Plant and Soil 219: 147-151.

Stangoulis, J.C.R. and Graham, R.D. (2007). Boron and plant disease. p. 207-214. In L.E. Datnoff, W.H. Elmer and D.M. Huber (eds.), *Mineral Nutrition and Plant Disease*. APS Press, Wisconsin.

Stevenson, F.J. (1991). Organic matter-micronutrient reactions in plants. p. 145-186. In J.J. Mortvedt, F.R. Cox, L.M. Shuman and R.M. Welch (eds.), *Micronutrients in*

Agriculture 2nd ed., SSSA Book Series No. 4. Soil Science Society of America, Madison, Wisconsin.

Stevenson, F.J. and Cole, M.A. (1999). *Cycles of Soil. Carbon, Nitrogen, Phosphorus, Sulfur and Micronutrients*. 2nd ed. John Wiley and Sons, New York.

Stewart, M. (2006). Conserving resources and building productivity. Case for fertilizer BMPs. Better Crops 90: 4-6.

Stoltzfus, R.J. and Dreyfuss, M.L. (1998). Guidelines for the use of iron supplements to prevent and treat iron deficiency anemia. International Nutritional Anemia Consultative Group (INACG), ILSI Press, Washington DC. www.ilsi.org/750210webbook.pdf.

Stone, E.L. (1990). Boron deficiency and excess in forest trees: a review. Forest Ecology and Management 37: 49-75.

Streeter, T.C., Rengel, Z., Neate, S.M. and Graham, R.D. (2001). Zinc fertilisation increases tolerance to *Rhizoctonia solani* (AG8) in *Medicago truncatula*. Plant and Soil 228: 233-242.

Suri I.K. (2005). A new technique for manufacturing of zincated urea. Indian Journal of Fertilisers 1: 59-61.

Surridge, C. (2004). Feast or famine? Nature 428: March 25, 360-361.

Sylvester-Bradley, R. (1985). Revision of a code for stages of development in oilseed rape (*Brassica napus* L.). Aspects of Applied Biology 10: 395-400.

Takkar, P.N., Chibba, I.M. and Mehta, S.K. (1989). *Twenty Years of Coordinated Research on Micronutrients in Soils and Plants*. Indian Institute of Soil Science, Bhopal.

Teixeira, I.R., de Souza, C.M., Borém, A. and da Silva, G.F. (2003). Variation of pH values and contents of organic carbon, copper, manganese, zinc and iron in depth in an Ultisol (Argissolo Vermelho-Amarelo) as function of different tillage systems. Bragantia 62: 119-126.

Thirunarayanan, K., Zimdahl, R.L. and Smika, D.E. (1985). Chlorsulfuron adsorption and degradation in soil. Weed Science 33: 558-563.

Thompson, J.P. (1990). Soil sterilization methods to show VA-mycorrhizae aid P and Zn nutrition of wheat in Vertisols. Soil Biology and Biochemistry 22: 229-240.

Thongbai, P., Hannam, R.J., Graham, R.D. and Webb, M.J. (1993). Interaction between zinc nutritional status of cereals and *Rhizoctonia* root rot severity. Plant and Soil 153: 207-214.

Tiller, K.G. and Merry, R.H. (1981). Copper pollution of agricultural soils. p. 119-140. In J.F. Loneragan, A.D. Robson and R.D. Graham (eds.), *Copper in Soils and Plants*. Academic Press, Sydney.

Tiwari, K.N. and Dwivedi, B.S. (1990). Response of eight winter crops to zinc fertilizer on a Typic Ustochrept soil. Journal of Agricultural Science (Cambridge) 115: 383-387.

Tsadilas, C.D. and Chartzoulakis, K.S. (1999). Boron deficiency in olive trees in Greece in relation to soil boron concentration. Acta Horticulturae 474: 341-344.

Tsadilas, C.D., Yassoglou, N., Kosmas, C.S. and Kallianou, C. (1994). The availability of soil boron fractions to olive trees and barley and their relationships to soil properties. Plant and Soil 162: 211-217.

Turnlund, J.R. (1999). Copper. p. 241-252. In M. Shils, J.A. Olson, M. Shike and A.C. Ross (eds.), *Nutrition in Health and Disease*. 9th ed. Williams & Wilkins, Baltimore.

Uauy, R., Olivares, M. and Gonzalez M. (1998). Essentiality of copper in humans. American Journal of Clinical Nutrition 67(5 Suppl): 952S-959S.

Underwood, E.J. and Suttle, N.F. (1999). *The Mineral Nutrition of Livestock*. CABI Publishing, New York.

UNIDO and IFDC (1998). *Fertilizer Manual*. Kluwer Academic Publishers, Boston.

Uren, N.C. (1999). Manganese. p. 287-294. In K. Peverill, L. Sparrow and D.J. Reuter (eds.), *Soil Analysis. An Interpretation Manual*. CSIRO Publishing, Melbourne.

USFNB (2001). *Dietary Reference Intakes for Vitamin A, Vitamin K, Arsenic, Boron, Chromium, Copper, Iodine, Iron, Manganese, Molybdenum, Nickel, Silicon, Vanadium, and Zinc*. US Food and Nutrition Board, National Academy Press, Washington.

Van Campen, D.R. (1991). Trace elements in human nutrition. p. 663-701. In J.J. Mortvedt, F.R. Cox, L.M. Shuman and R.M. Welch (eds.), *Micronutrients in Agriculture*. 2nd ed. SSSA Book Series No. 4. Soil Science Society of America, Madison, Wisconsin.

van der Waals, J.H. and Laker, M.C. (2008). Micronutrient deficiencies in crops in Africa with emphasis on Southern Africa. p. 1-40. In B.J. Alloway (ed.), *Micronutrient Deficiencies in Global Crop Production*. Springer, Dordrecht.

Verstraeten, S.V., Lanoue, L., Keen, C.L. and Oteiza, P.I. (2005). Relevance of lipid polar headgroups on boron-mediated changes in membrane physical properties. Archives of Biochemistry and Biophysics 438: 103-110.

Viets, F.G. Jr and Lindsay, W.L. (1973). Testing soils for zinc, copper, manganese and iron. p. 153-172. In L.M. Walsh and J.D. Beaton (eds.), *Soil Testing and Plant Analysis*, Revised ed. Soil Science Society of America, Madison, Wisconsin.

Vlamis, J. and Ulrich, A. (1971). Boron nutrition in the growth and sugar content of sugar beet. Journal American Society of Sugar Beet Technology 16: 428-439.

Vlek, P. (ed.) (1985). *Micronutrients in Tropical Food Crop Production*. M. Nijhoff/W. Junk Publishers, Dordrecht.

Vose, P.B. (1982). Iron nutrition in plants: A world overview. Journal of Plant Nutrition 5: 233-249.

Walker, C.F. and Black, R.E. (2004). Zinc and the risk for infectious disease. Annual Review of Nutrition 24: 255-275.

Wang, K., Xu, J.M., Wei, Y.Z., Yang, Y. and Bell, R.W. (1997). The influence of boron fertilizer on distribution of extractable boron in soil profiles in rape rice rotations in south east China. p. 57-61. In R.W. Bell and B. Rerkasem (eds.), *Boron in Soils and Plants*, Development in Plant and Soil Sciences 76. Kluwer Academic Publishers, Dordrecht.

Wang, K., Yang, Y., Xue, J.M., Ye, Z.Q., Wei, Y. and Bell, R.W. (1999). Low risks of toxicity from boron fertiliser in oilseed rape-rice rotations in south east China. Nutrient Cycling in Agro-ecosystems 54: 189-197.

Wang, Y.J., Zhou, D.M., Sun, R.J., Cang, L. and Hao, X.Z. (2006). Cosorption of zinc and glyphosate on two soils with different characteristics. Journal of Hazardous Materials A137: 76-82.

Wang, Z., Shan, X. and Zhang, S. (2002). Comparison between fractionation and bioavailability of trace elements in rhizosphere and bulk soils. Chemosphere 46: 1163-1171.

Warington, K. (1923). The effect of boric acid and borax on the broad bean and certain other plants. Annals of Botany 27: 629-672.

Wei, Y., Bell, R.W. and Yang, Y. (2002). Prognosis of boron deficiency in oilseed rape (Brassica napus) by soil analysis. p. 311-317. In H. E. Goldbach, B. Rerkasem, M. A. Wimmer, P. H. Brown, M. Thellier and R. W. Bell (eds.), *Boron in Plant and Animal Nutrition*. Kluwer Academic Publishers, Dordrecht.

Wei, Y.Z., Bell, R.W., Yang, Y., Ye, Z.Q., Wang, K. and Huang, L. (1998). Prognosis of boron deficiency in oilseed rape (*Brassica napus* L.) by plant analysis. Australian Journal of Agricultural Research 49: 867-874.

Welch, R.M. (1999). Effects of nutrient deficiencies on seed production and quality. Advances in Plant Nutrition 2: 205-247

Welch, R.M. (2001). Micronutrients, agriculture and nutrition: linkages for improved health and well being. p. 247-290. In K. Singh, S. Mori and R.M. Welch (eds.), *Perspectives on the Micronutrient Nutrition of Crops*, Scientific Publishers (India), Jodhpur.

Welch, R. M. (2005). Harvesting health – the future of agriculture. p. 4-5. In C.J. Li, F.S. Zhang, A. Dobermann, P. Hinsinger, H. Lambers, X.L. Li, P. Marschner, L. Maene, S. McGrath, O. Oenema, S.B. Peng, Z. Rengel, Q.R. Shen, R. Welch, N. Von Wiren, X.L. Yan and Y.G. Zhu (eds.), *Plant Nutrition for Food Security, Human Health and Environmental Protection*. Proceedings of the XVth International Plant Nutrition Colloquium, 9-13 September 2005, Beijing. Tsinghua University Press, Beijing.

Welch, R.M. (2008). Linkages between trace elements in food crops and human health. p. 287-309. In B. J. Alloway (ed.), *Micronutrient Deficiencies in Global Crop Production*. Springer, Dordrecht.

Welch, R.M and Graham, R.D. (2005). Agriculture: the real nexus for enhancing bioavailable micronutrients in food crops. Journal of Trace Elements in Medicine and Biology 18: 299-307.

Welch, R.M., Allaway, W.H., House, W.A. and Kubota, J. (1991). Geographic distribution of trace element problems. p. 31-57. In J.J. Mortvedt, F.R. Cox, L.M. Shuman and R.M. Welch (eds.), *Micronutrients in Agriculture*, 2nd ed. SSSA Book Series No. 4. Soil Science Society of America, Madison, Wisconsin.

Westerman, R.L. (ed.) (1990). *Soil Testing and Plant Analysis*, 3rd ed. SSSA Book Series No. 3. Soil Science Society of America, Madison, Wisconsin.

Westfall, D.G., Mortvedt, J.J., Peterson, G.A. and Gangloff, W.J. (2005). Efficient and environmentally safe use of micronutrients in agriculture. Communications in Soil Science and Plant Analysis 36: 169-182.

White, J.G. and Zasoski, R.H. (1999). Mapping soil micronutrients. Field Crops Research 60: 11-26.

WHO (2002). *The World Health Report 2002. Reducing Risks, Promoting Healthy Life*. WHO, Geneva.

Wild, A. and Mazaheri, A. (1979). Prediction of the leaching rate of boric acid under field conditions. Geoderma 22: 127-136.

Wild, A., Jones, L.H.P. and MacDuff, J.H. (1987). Uptake of nutrients and crop growth: the use of flowing nutrient solutions. Advances in Agronomy 41: 171-219.

Williams, C.M.J., Maier, N.A. and Barlett, L. (2004). Effect of molybdenum foliar sprays on yield, berry size, seed formation, and petiolar nutrient composition of 'Merlot' grapevines. Journal of Plant Nutrition 27: 1891-1916.

Wong, M.T.F., Bell, R.W. and Frost, K. (2005). Mapping boron deficiency risk in soils of south-west Australia using a weight of evidence model. Australian Journal of Soil Research 43: 811-818.

Wood, B.W., Reilly, C.C. and Nyczepir, A.P. (2004). Mouse ear of pecan: A nickel deficiency. Hortscience 39: 1238-1242.

Wood, I.J. and Myers, R.J.K. (1987). Food legumes in farming systems in the tropics and subtropics. p. 34-45. In E.S. Wallis and D.E. Byth (eds.), *Food Legume Improvement for Asian Farming Systems*. Australian Centre for International Agricultural Research, Canberra.

Wood, M.J. and Robson, A. D. (1984). Effect of copper deficiency in wheat on the infection of roots by *Gaeumannomyces graminis* var. tritici. Australian Journal of Agricultural Research 35: 735-742.

Xu, F., Goldbach, H.E., Brown, P.H., Bell, R.W., Fujiwara, T., Hunt, C.D., Goldberg, S. and Shi, L. (eds.) (2007). *Advances in Plant and Animal Boron Nutrition*. Springer, Dordrecht.

Xu, J.M., Wang, K., Huang, L. and Bell, R.W. (2001). Soil boron fractions and their relation to boron availability to oilseed rape. Soil Science Society of America Journal 65: 133-138.

Yang, X., Yu, Y.G., Yang, Y., Bell, R.W. and Ye, Z.Q. (2000). Residual effectiveness of boron fertilizer for oilseed rape in intensively cropped rice-based rotations. Nutrient Cycling in Agro-ecosystems 57: 171-181.

Yermiyahu, U., Keren, R. and Chen, Y. (2001). Effect of composted organic matter on boron uptake by plants. Soil Science Society of America Journal 65:1436-1441.

Yeung, C.K., Glahn, R.P., Welch, R.M. and Miller, D.D. (2005). Prebiotics and iron bioavailability - is there a connection? Journal of Food Science 70: R88-R92.

Yilmaz, A., Ekiz, H., Torun, B., Gultekin, I., Karanlik, S., Bagci, S.A. and Cakmak, I. (1997). Effect of different zinc application methods on grain yield and zinc concentration in wheat cultivars grown on zinc-deficient calcareous soils. Journal of Plant Nutrition 20: 461-471.

Yilmaz. A., Ekiz, H., Gültekin, I., Torun, B., Barut, H., Karanlik, S. and Cakmak, I. (1998). Effect of seed zinc content on grain yield and zinc concentration of wheat grown in zinc-deficient calcareous soils. Journal of Plant Nutrition 21: 2257-2264.

Yip, R. and Dallman, P.R. (1996). Iron. p. 278-292. In E.E. Ziegler and L.J. Filner (eds.), *Present Knowledge in Nutrition*, 7th ed. ILSI Press, Washington DC.

Zarcinas, B.A. and Nable, R.O. (1992). Boron and other impurities in South Australian fertilizers and soil amendments. CSIRO Division of Soils Report No. 118. CSIRO, Melbourne.

Zerrari, N., Moustaoui, D. and Verloo, M. (1999). The various forms of soil boron: importance, effect of soil characteristics and plant availability. Agrochimica 43: 77-88.

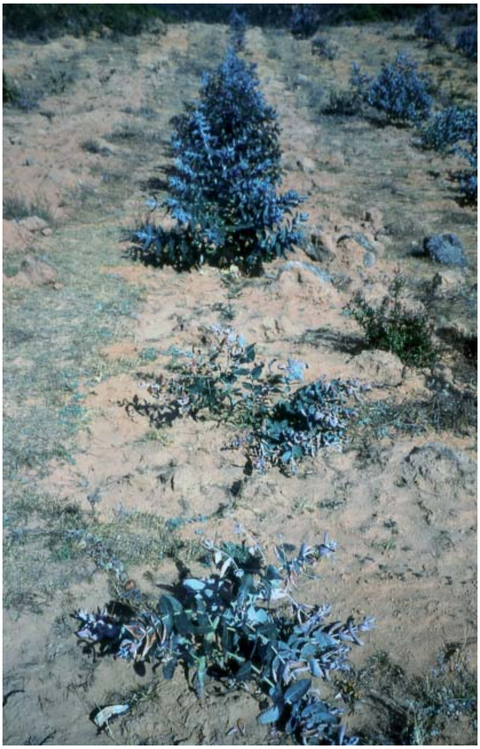
Zhang, F.S., Römheld, V. and Marschner, H. (1991). Diurnal rhythm of release of phytosiderophores and uptake rate of zinc in iron-deficient wheat. Soil Science and Plant Nutrition 37: 671-678.

Zou, C., Gao, X., Shi, R., Fan, X. and Zhang, F. (2008). Micronutrient deficiencies in crop production in China. p. 127-148. In B. J. Alloway (ed.), *Micronutrient Deficiencies in Global Crop Production*. Springer, Dordrecht.

13. Plates on micronutrient deficiency symptoms

B deficiency in coffee (Thailand, B. Dell)

Hollow-heart in B-deficient peanut kernels (Australia, R.W. Bell)



B deficiency in bluegum, two trees in the foreground (China, B. Dell)

B deficiency in rapeseed (China, R.W. Bell)

B deficiency in pomelo (Thailand, B. Dell)

Fe deficiency in cassava (Thailand, B. Dell)

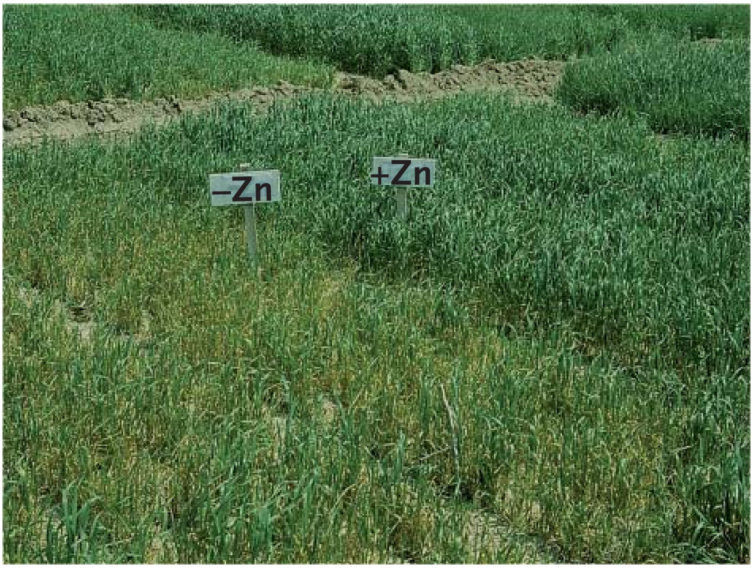
Fe deficiency in nectarine (Spain, J.J. Lucena)

Fe deficiency in orange (China, F.S. Zhang)

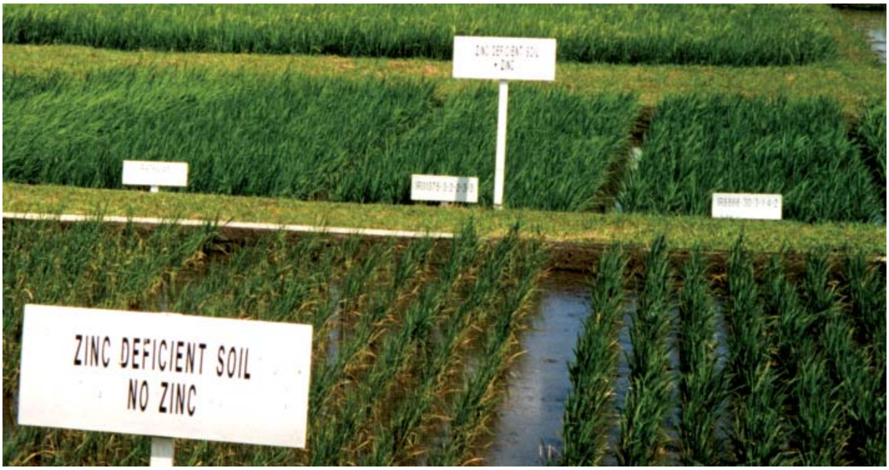
Fe deficiency in apple (Spain, J.J. Lucena)

Zn deficiency in corn field (USA, R. Gehl)
Inset : Zn deficiency symptoms (China, F.S. Zhang)

Zn deficiency in pecan (USA, B. Wood)



Zn deficiency in wheat (Turkey, I. Cakmak)



Screening for Zn efficiency in rice: rear plots +Zn, front plots of the same cultivars without Zn (Philippines, R.W. Bell)

Cu deficiency in peanut (Thailand, R.W. Bell)

Mn deficiency in soybean (USA, R. Gehl)

Mo deficiency in chickpea – the rear field has been supplied with Mo on the seed coat (Bangladesh, C. Johansen)

Ni deficiency in pecan (USA, B. Wood)